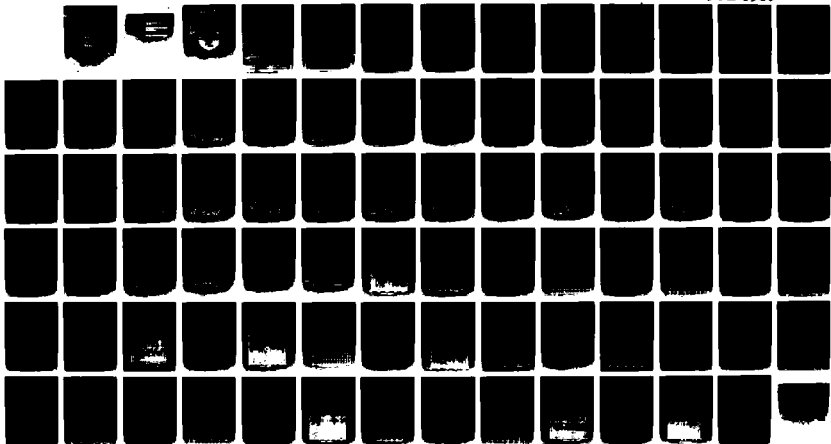


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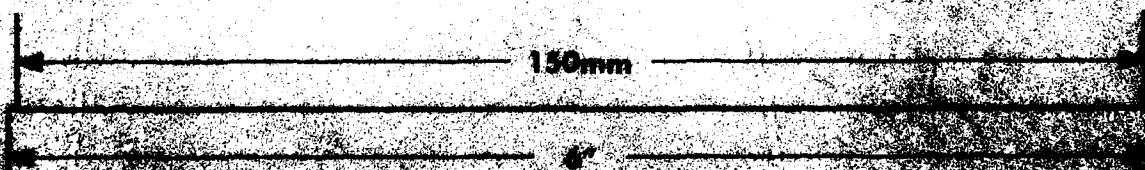
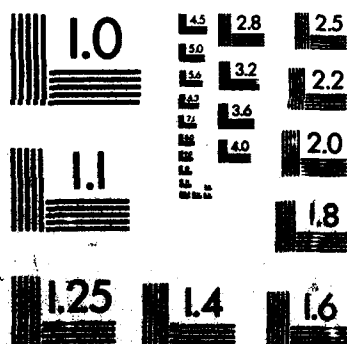
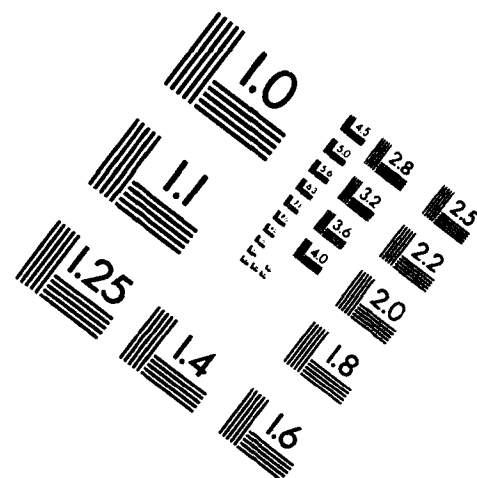
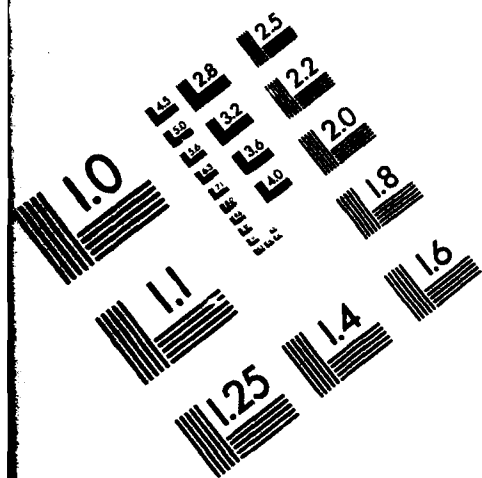
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July 1989

Photoelectron Pumped Phosphors

San Diego State University Foundation

NAVAL OCEAN SYSTEMS CENTER

San Diego, California 92152-5000

E. G. SCHWEIZER, CAPT, USN
Commander

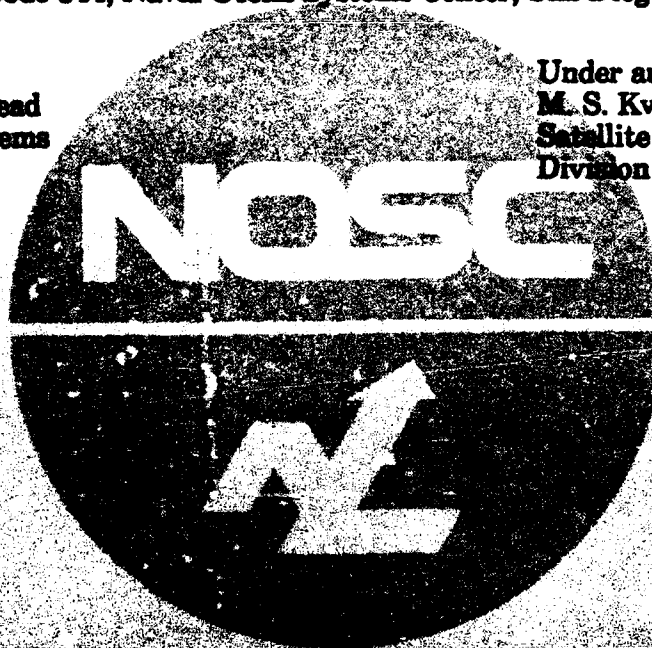
R. M. HILLYER
Technical Director

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<p>The reported investigation of cathodophosphors was undertaken in connection with the development of optical devices for the detection of long wavelength photons in which the initial photon-to-electron detection is performed by an optical diode, then the photoelectrons being accelerated by the electric field penetrate into a phosphor screen and the screen produces multiple photons which are detected by a (close coupled) photomultiplier.</p> <p>This report presents the results of a comprehensive analysis and systematization of the data relevant to the fast and very fast commercially available phosphors and developmental works on improved materials and processes in the field of phosphors, especially cathodophosphors.</p> <p>The investigation included analysis of II-VI phosphors, alkaline-earth chalcogenides, silicates, garnets, halides, and some ternary compounds with diamond-like crystal structure. The investigation included, also, analysis of data regarding the activators and coactivators as well as mixtures of phosphors with optically transparent conductive powders for the low-energy-electron cathodophosphors.</p> <p>The report includes the tables and diagrams with the phosphors' parameters, namely, their chemical composition, brightness and its drop rate, cathodoluminescence efficiency, and persistence.</p>					
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1. Introduction

This report spans the period from April 25, 1987 to January 31, 1988. The work has been done in accordance with the Contract N66001-85-D-0203, Delivery Order 0045, and consists mainly of a literature survey of available cathodophosphors, analysis of developmental work in progress in the field of cathodophosphors, and recommendations regarding improved optical phosphors for further research.

The need in the reported research is connected to development of the optical devices for the detection of the 1.39 and 1.45eV photons of the far-red part of the spectrum. The device uses an optical diode for the initial photon-to-electron detection; the diode serves also as a cathode in a cathode ray tube where a phosphor screen functions as an anode. The applied electric field accelerates the photoelectrons into the phosphor that produces multiple photons which are detected by a photomultiplier tube. In such a hibride device, the phosphor parameters to a substantial degree, control the overall efficiency of the device.

The report consists of a general review of the luminescence materials which includes the basic physical concepts of the phosphors for different applications, and the following detailed description of the different groups of cathodoluminophors; special attention has been paid to the developmental work on improved materials and processes. The basic characteristics of some commercially available short and very short decay time cathodophosphors are presented in the Appendix.

2. Cathodoluminescence and Recombination Luminescence

In general, cathodoluminescence (CL) is the luminescence that appears as a result of bombardment of a phosphor (PH) by an electron beam. A flux of electrons from a cathod is accelerated by the electric field and penetrates into a screen which is a thin but dense layer of a luminophore (LP) that is deposited on a transparent substrate. CL is usually observed from the layer side opposite to the bombarding beam. The decelerating electrons of the beam give their kinetic energy to the crystal lattice of the LP. Most part of the energy (up to 90%) is transformed into heat; the rest of it is used for excitation of CL and for secondary electron emission (SEE) from the screen.

Specific features of CL relate to the way of delivery of energy to the LP and to the secondary electric effects [1-3], namely: (i) The electron energy is absorbed by the entire crystal lattice and is transferred along it to the centers of luminescence. Therefore, the indirect excitation of the centers predominant; only about 1% of all luminescence is related to the direct excitation of the centers. (ii) The bombarding electrons lose their kinetic energy in a thin layer of LP (for electrons with energy 10 keV, the thickness is about 2.5 μm). The density of excitation, which is measured with the electron energy per unit of volume of LP per unit of time, and consequently the brightness of CL may have exclusively high magnitudes unattainable for other methods of the LP excitation. (iii) The CL brightness has a very strong dependence upon dynamics of the charges on the surface of the screen which appear there as a result of SEE, if the screen is made from a dielectric or a semiconductor with a high resistivity. The CL brightness depends on the energy of the bombarding electrons and the beam current density.

For initiation of CL, it is enough to have the energy of a few eV. But up to 120-140 V, radiation is unstable, because (as a result of small coefficient of the secondary electron emission, SEE, [$\sigma < 1$]) the screen acquires a negative charge and repulses the electron beam. At the potentials up to 10-12 kV, $\sigma > 1$ and potential of the screen automatically approaches the

potential of the accelerating electrode because of the release of the secondary electrons. In this range of energy, CL is stable, and brightness is proportional to the square of voltage because the depth of penetration of electrons in LP is proportional to the square of their energy. Dependence of brightness, B , on voltage, V , in this range can be described by the expression

$$B = kI (V - V_0)^p, \quad (1)$$

where coefficient of proportionality, k , and parameter $p = 2$ depend on the LP composition and properties of the screen; I is the current density of the electron beam, and V_0 is the minimal potential an electron needs to pass the nonactive surface layer of LP. Deviation from Eqn. (1) at low voltages is caused by relatively high losses on SEE. At voltages that are too high, the depth of the electron penetration is growing, the SEE coefficient σ is again < 1 , potential of the screen is close to the cathode potential, energy of the electrons which approach the LP is decreasing, and B again lags V . The greater is V , the slower is the growth of B as V increases. The ranges of V where LP does not follow the Eqn. (1) depend on the LP composition and the screen technology. It is possible to decrease the influence of the screen charge at high voltages by deposition of a thin ($0.1 \mu\text{m}$) layer of aluminum on the screen surface from the beam side. The film discharges the screen surface, is quite transparent for the high energy electrons, and the losses for the film breakdown are compensated to some degree by the mirror reflection of the screen luminescence. Brightness of CL is proportional to I , but at the high currents, the saturation of B is observed. The saturation may be caused by the limited amount of the radiating centers, if the activator concentration is small or the time of their excited state is too long. The CL efficiency is never greater than 20% and usually lays within the limits of 1% to 10%. Nevertheless, at the relatively high V and I , instantaneous brightness may reach exclusively high magnitudes up to 10^9 nit (10^5 stb).

In the LP's with the centers of luminescence of one type, the CL spectrum is similar to the photoluminescence (PL) spectrum. If the centers are of different types, the total irradiance of CL may be substantially different. As a result of the high excitation density, the irradiance includes additional bands not observable at low excitation. Moreover, because of specifics of

the absorption and radiation mechanisms, the intensity distribution between the bands may be totally different in comparison with other excitation methods.

The high excitation density connected to the small depth of the bombarding electron penetration causes some other specifics of CL. The persistence of radiation spans the range from a fraction of μsec to a few seconds. Nevertheless, the processes of shorter duration dominate independent of the persistence: on initial stage of the process of luminescence increase or decrease, dependence of brightness on time is close to the exponential one. The temperature depreciation of CL takes place at higher temperatures than those of a photoluminophor (PL). But, chemical changes and destruction of LP's by the electron beams appear much faster in CL than with other excitation methods. At low accelerating voltages and high currents, the LP demonstrate reversible depreciation and a temporary decrease of brightness. At high power, the depreciation is replaced by a nonreversible decay with chemical decomposition of the material and a sharp brightness decrease. Increase of the voltage weakens and increase of the current density intensifies the screen fatigue.

Recombination Luminescence (RL) appears as the result of recombination of particles which were separated in the process of excitation. RL of semiconductors is the result of recombination of electrons and holes with the lattice defects on which they were located prior to the excitation [4], and also as the result of recombination of free electrons with free holes [5]. If RL of a solid belongs to the visible or UV parts of the spectrum, the material is called crystallophosphor (CP) or phosphor.

The RL intensity depends on the product of the concentrations of the recombining particles, C_1 and C_2 . If $C_1 = C_2$, brightness follows the formula

$$B = B_0 (1 + at)^{-2} \quad (2)$$

where B_0 is B at the moment of the excitation discontinuance ($t = 0$), a is a constant that depends on the nature of material and the excitation intensity (a increases with the intensity increase). If $C_1 \gg C_2$,

$$B = B_0 \exp(-t/\tau) \quad (3)$$

where τ is the lifetime of the minority particles. Nevertheless, in real systems such simple relations between B and t may be observed quite rarely because of some complicating circumstances. For example, in semiconductors there are different kinds of traps that may hold electrons and/or holes for relatively long periods of time. This slows down the process of luminescence and makes this process dependent on temperature, because the release of charges from the traps needs a certain activation energy. If the CP temperature is increasing during the process of excitation, the brightness may be increasing as the result of release of a great number of particles from the traps. On the other hand, these traps may themselves be the centers of recombination, although some of them may not produce recombination radiation. The number of the acts of RL on different kinds of traps depends on the method and intensity of excitation. Therefore, the rate of RL is often independent from the intensity.

In many real crystals, brightness of RL may be approximately described by Becquerel's formula

$$B = B_0 (1 + at)^{-\alpha} \quad (4)$$

where α is an empirical constant. Nonetheless, at large t , B is almost independent on B_0 .

3. General Review of Phosphors (Luminophors)

3.1. Photoluminophors

For luminescent lamps of low pressure, a mixture of $MgWO_4$ (blue) and $(Zn, Be)_2SiO_4:Mn$ (yellow-red) was initially used. It was replaced by a monocomponent system of calcium halophosphate $3Ca_3(PO_4)_4 \cdot Ca(F, Cl)_2:Sb, Mn$ which had red radiation deficiency. For improvement, the mixture of $CaSiO_3:Pb, Mn$ (Red) and $Zn_2SiO_4:Mn$ (green) may be added. An improvement can be achieved also by addition of $6MgO \cdot As_2O_5:Mn$ and $(Sr, Mg)_3(PO_4)_2:Sn$ with red radiation. For lamps with radiation in the UV part of the spectrum, $BaSiO_3:Pb$ and $(Sr, Ca)_3(PO_4)_2:Tl$ ($\lambda = 250-360$ nm), and $(Ca, Zn)_3(PO_4)_2:Tl$ and $(Ca, Mg)_3(PO_4)_2:Tl$ (so called, erythema lamps, $\lambda = 290-300$ nm) are used. For the mercury lamps of high and superhigh pressure, the mixture of $6MgO \cdot As_2O_5:0.01Mn$; $3.5MgO \cdot 0.5MgF_2 \cdot GeO_2:0.01Mn$; $BaO \cdot SrO \cdot Li_2O \cdot 2.2SiO_2:0.3Ce \cdot 0.07Mn$;

$(\text{Sr}, \text{Zn})_3(\text{PO}_4)_2:\text{Sn}$ is commonly used. These phosphors give red radiation under UV excitation and do not decrease their radiation at high temperature in the lamp.

The longest afterglow characterizes sulfides of the alkali-earth metals (CaS, SrS) activated by Cu , Bi , Pb , rare earth elements (REE), etc. But these phosphors are unstable in the air and are difficult for hermetization. Phosphors on the basis of ZnS are widely used. Most bright yellow-green luminescence is typical for $\text{ZnS}:\text{Cu}$. The lower initial brightness, but even longer luminescence, is typical for $\text{ZnS}:\text{Cu}, \text{Co}$.

3.2 Cathodoluminophors

The brightest blue phosphor is $\text{ZnS}:\text{Ag}$ (energy yield of luminescence up to 20%); for white screens its mixture with $\text{ZnS}:\text{CdS}:\text{Ag}$ (yellow) is used. A vast amount of cathodoluminophors is developed on the basis of silicates, tungstates, oxides, aluminates, etc. For the cathode-ray tubes with afterglow, good results can be achieved with the two-layer screens: 73% ZnS -27% CdS : 0.004% Cu (lower layer) and $\text{ZnS}:\text{0.015Ag}$ (upper layer).

3.3. Electroluminophors (EL)

Basically, only $\text{ZnS}:\text{Cu}$ has a practical value. In contrast with other luminophors, the copper concentration in EL's is higher (up to 1 mg of Cu per 1 g of ZnS) [3]. Coactivators, such as Mn , Ag , Pb , Sb , Ga , Al , and Cl may be added for the brightness increase and change of the luminescence spectrum. The other matrix materials for ELs are $(\text{Zn}, \text{Cd})\text{S}$, $\text{Zn}(\text{S}, \text{Se})$, SiC (on which electroluminescence was first discovered in 1923 [6]), and some other inorganic and organic materials (a complete bibliography see in [7]).

3.4. Activators

Activators (Ac) are the chemical elements that are introduced in the crystal lattice in the process of preparation of a crystallophosphor (CP). Atoms of Ac, together with surrounding atoms of matrix crystal lattice and sometimes together with lattice defects (e.g. vacancies) and/or other impurities (coactivators, CA),

form centers of luminescence of CP. In many cases, luminescence of a crystal is a direct consequence of presence of the Ac and CA, but there are also many crystals that produce luminescence without Ac and CA (recombination radiation, exciton radiation).

An activator absorbs energy of excitation or capturing energy absorbed by the matrix lattice, and then releases it in the form of radiation. It is still not exactly known why an atom may be a good Ac for a given crystal. The luminescence spectrum usually is typical for each Ac in a given crystal lattice. In some cases, it is possible to find similarity between the absorption and luminescence spectra of an Ac in a crystal lattice and the spectra of the same atoms (ions) in the free state. If there are several Ac in a CP, the spectrum of luminescence in the simplest case consists of bands related to each Ac. Nevertheless, intensity of the bands depends not only on the related Ac contents, but also on the energy exchange between the Ac, on temperature, and on the intensity of the excitation light. In some cases, the interaction of Ac takes place with formation of more complex luminescence centers.

Presence of Ac in a crystal may be revealed at as low concentrations as 10^{-7} . In Table 1 there are main Ac for some types of CP (the order of optimal concentrations, i.e. giving maximum luminescence brightness, is presented in parentheses).

The activator choice is so far almost totally empirical and needs a detailed theoretical and experimental investigation.

3.5 On the Deposition Technique

In a majority of applications of cathodophosphors the powder of CP has to be deposited on a substrate, usually a glass. The methods of deposition may be separated into two groups, namely, printing methods and sedimentation methods (see, e.g. [99]). It is quite common to use an organic binder, usually acetone or (polyvinyl) alcohol, with or without some dopants. After deposition, the binder is burned out in air [28, 143] at 400° - 500° C. Another binder that has found wide use is a solution of $K_2O \cdot nSiO_2$ (the authors of [70] applied $n = 3.9$ while in [144] $n = 1$). The best results are

Table 1. Basic Activators of the Most Used Crystallophosphors V [50, Chapter 7; 8, Sec. 48-51]

Matrix Material of Luminophor	Activators
Zinc sulfide, ZnS	Cu(5×10^{-5} - 10^{-4}) [coactivators Pb(10^{-6}), Co($<10^{-6}$), Ni(10^{-7} , Al, Ga]; Ag(10^{-4}), Au(10^{-4}), Mn(10^{-3}), rare- earth elements (REE) (10^{-3} - 10^{-4}), P, As
Alkaline-earth sulfides (CaS, SrS, BaS)	Bi(10^{-4}), REE(Sm+Eu, Sm+Ce), Bi+Cu, Bi+Pb
Silicates	Mn (up to 10^{-2})
Halophosphates	Mn & Sb
Alkali halides (e.g., KCl, NaI, CsI)	Tl(10^{-3}), In, Ga, Ni, Cu, Ag, Sn, Pb, Ge, Eb
Fluorite (CaF ₂)	REE

K_2SiO_3 . The solution is mixed with a phosphor and the mixture is applied to the glass. If the first application is not satisfactory, it may be repeated after spraying 2% K_2SiO_3 solution on the surface of the first layer.

The choice of the deposition method depends on the phosphor chemical composition and the substrate material. Some phosphor may be subject to hydrolysis; in this case, pH of the sedimentation solution has to be thoroughly controlled by addition of, say, KOH or by replacement of a polyvinyl alcohol with a more base solvent.

3.6 Conclusion

At the moment, there is known to be a substantial amount of phosphors and data regarding their properties, recommendations of the optimal activators and coactivators (see Section 4). Nevertheless, the problem of choosing the best phosphor for a certain practical use is still far from a solution. The main reason for it lays in the multitude of parameters that characterize a phosphor. For example, for a cathodoluminophor, its luminescence spectrum, persistence characteristics, luminous efficiency, energy efficiency, rate of depreciation, dependence of parameters on the cathod ray energy, may be considered as the minimum information for choice of a proper material. But for some use, the size of grains, uniformity of the activator (and/or coactivator) distribution in the grains, sorts, concentration and distribution of lattice defects in the grains, existence and thickness of a non-luminescent light absorbing layers on the surface of the single-crystalline grains may be an additional group of parameters, and their variations will control the effectiveness of a cathodoluminophor which otherwise would be the best choice.

The multiplicity of parameters makes it difficult to develop an adequate theoretical model of the processes that take place in a cathodoluminophore.

The process of collision of an electron with a phosphor grain has a statistical character and may be described at ideal conditions by Poisson's distribution, namely, the probability of collision of n electrons with a unit area of the target A is

$$P(N,n) = \frac{N!}{n!(N-n)!} A^{-n}(1-A^{-1})^{N-n}$$

where N is a total amount of electrons approaching the target. The best experimental magnitudes of P (see, for example [9]) are about five times smaller than theoretical ones. Understanding of the processes that take place when an electron penetrates in a cathodoluminophor evidently cannot be considered as satisfactory and needs following detailed theoretical and experimental study at various physical and chemical conditions.

4. "Standard" Cathodoluminophors

The CL standardization is the function of the Tube Engineering Panel Advisory Council (TEPAC) of the Electronic Industries Association (EA) [10]. Currently, the optical characteristics of cathode ray tube screens are the contents of the EIA TEPAC Publication No. 116A. The current list of the standard phosphors includes 114 compounds that differ by their spectral composition, chemical contents, and persistent characteristics. This report includes only short and very short radiating phosphors (decay time to 1/10 of initial brightness is from 1 to 10 μ s for former and less than 1 μ s for latter). Only 14 phosphors enter this time category. Table 2 and diagrams of Appendix 1 present spectral and persistent characteristics of the 14 phosphors. It is important to mention that the 14 phosphors have a relatively low luminous (lumen/W) and energy (W/W) efficiency (see Tables 3, 4, 5 [11]) of cathodoluminescence. A possible explanation for this experimental result lays in the specifics of the phonon energy distribution in a crystal bombarded by relatively high energy electrons.

Investigations of phosphors, and particularly cathodoluminophors, are continuing to be pursued by specialists of many different branches of science and technology. Cathodoluminescence (CL) of activator-free single crystals of CsF, CsCl, CsBr, and CsI was investigated at different temperatures [14, 15] and showed a strong emission at near UV and violet parts of spectrum. CL of II/VI compounds, such as ZnO:Zn and ZnS:Cu,As [16], CdS_{1-x}Sr_xS:Ce [19] still attracts substantial interest, in spite of its long history. CL of elemental materials, such as diamond [19], is successfully used for

Table 2. Main Parameters of the Phosphors

Designation		Spectral Maximum nm	Color	Time to 10% of Init. Brightness ns	Chemical Formula
International	U.S.				
AA	P16	380	Violet &	120	$(\text{Ca}, \text{Mg})_2\text{SiO}_4:\text{Ce}$
BA	--	400	Purplish-blue	320	--
BC	--	430	Violet	--	$\text{ZnS}:\text{Ag}, \text{Al}$
BD	--	400	Blue	<100	$\text{ZnS}:\text{Ag}, \text{Ni}$
BH	P47	390	Purplish-blue	82	$\text{Y}^2\text{SiO}_4:\text{Ce}$
BK	P37	465	Greenish-blue	160	$\text{ZnS}:\text{Ag}, \text{Ni}$
GE	P24	510	Green	1500	ZnO
GG	P15	392(505)*	Green	2800	ZnO
GS	--	525	Yellowish-green	950	$\text{ZnCdS}:\text{Ag}, \text{Ni}$
GT	--	480	Bluish-green	900	$\text{ZnCdS}:\text{Ag}, \text{Ni}$
GU	--	420(520)*	White	210	$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}/\text{Y}_2\text{SiO}_4:\text{Ce}$
KF	P36	550	Yellow-green	250	$\text{ZnCdS}:\text{Ag}, \text{Ni}$
KG	P46	530	Yellow-green	160	$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$
KH	P48	525(390)*	Yellow-green	124	$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}/\text{Y}_2\text{SiO}_4-7/3$

*Number in parentheses relates to a second (lower) maximum.

Table 3. Chemical Composition of Phosphors

P Number	Chemical Composition
P-1	$\text{Zn}_2\text{SiO}_4:\text{Mn}$
P-2	$\text{ZnS}:\text{Cu}$
P-3	$\text{ZnO} \cdot \text{BeO} \cdot \text{SiO}_2:\text{Mn}$
P-4	$\text{ZnS}:\text{Ag} + \text{ZnCdS}:\text{Ag}$
P-5	$\text{CaWO}_4:\text{W}$
P-6	$\text{ZnS}:\text{Ag} + \text{ZnCdS}:\text{Ag}$
P-7	$\text{ZnS}:\text{Ag} + \text{ZnCdS}:\text{Cu}$ (ZnS on ZnCdS)
P-10	KCL
P-11	$\text{ZnS}:\text{Ag}$
P-12	$\text{ZnMgF}_2:\text{Mn}$
P-13	$\text{MgSiO}_3:\text{Mn}$
P-14	$\text{ZnS}:\text{Ag} + \text{ZnCdS}:\text{Cu}$
P-15	$\text{ZnO}:\text{Zn}$
P-16	$2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2:\text{Ce}$
P-17	$\text{ZnO} + \text{ZnCdS}:\text{Cu}$
P-18	$\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_4:\text{Ti} + (\text{P-3})$
P-19	$\text{ZnF}_2:\text{Mn}$
P-20	$\text{ZnCdS}:\text{Ag}$
P-21	$\text{MgF}_2:\text{Mn}$
P-22G	$\text{Zn}_2\text{SiO}_4:\text{Mn}$; $\text{ZnCdS}:\text{Cu, Al}$; $\text{ZnS}:\text{Cu, Al, Au}$
P-22H	$\text{Zn}_3(\text{PO}_4)_2:\text{Mn}$; $\text{YVO}_4:\text{Eu}$; $\text{Y}_2\text{O}_3:\text{Eu}$; $\text{Y}_2\text{O}_3:\text{Eu}$
P-22B	$\text{ZnS}:\text{Ag}$

Table 3 (cont.).

P Number	Chemical Composition
P-23	ZnS:Ag+ZnCdS:Cu,Al
P-24	ZnO:Zn
P-25	CaSiO ₃ :Pb,Mn
P-26	KmGF ₃ :Mn
P-27	Zn ₃ (PO ₄) ₂ :Mn
P-29	P-2 + P-25
P-31	ZnS:Cu,Ag
P-32	CaS·MgO·SiO ₂ :Ti 2CaO·Al ₂ O ₃ ·SiO ₂ :Ce ZnCdS:Cu
P-33	KMgF ₃ ·MgF ₂ :Mn
P-34	ZnS:Cu,Pb
P-39	Zn ₂ SiO ₄ :Mn,As
P-40	ZnS:Ag (Blue) ZnCdS:Cu (Yellow)
P-42	P-31 + P-39
P-43	Gd ₂ O ₂ S:Tb
P-44	La ₂ O ₂ S:Tb
P-45	Y ₂ O ₂ S:Tb
P-46	Y ₃ Al ₅ O ₁₂ :Ce
P-47	Y ₂ SiO ₅ :Ce
P-48	P-46 + P-47

Table 3 (cont.).

P Number	Chemical Composition
P-49	$\text{Zn}_2\text{SiO}_4 + \text{YVO}_4$
P-50	$\text{Y}_2\text{O}_3:\text{Eu}$ (Red) $\text{ZnCdS}:\text{Cu},\text{Ni}$ (Green)
P-51	$\text{YVO}_4:\text{Eu}$ (Red) ; $\text{ZnCdS}:\text{Cu},\text{Ni}$ (Green)
P-52	$\text{ZnSiO}_4:\text{Ti}$
P-53	$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}$; $\text{Y}_3(\text{Al},\text{Ga})_5\text{O}_{12}:\text{Tb}$ (improved)
P-54	$\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ (Red) $\text{ZnS}:\text{Cu},\text{Al}$ (Green) $\text{ZnS}:\text{Ag} + \text{ZnS}:\text{Cu},\text{Al} + \text{Y}_2\text{O}_2\text{S}:\text{Eu}$ (White)
P-55	$\text{ZnS}:\text{Ag}$
P-56	$\text{Y}_2\text{O}_3:\text{Eu}$ (Red)
P-57	$\text{Zn}_2\text{SiO}_2:\text{Mn} + \text{KMgF}_3:\text{Mn}$

Table 4. Typical Efficiency and Aging Characteristics of Phosphors.

P-Number	Efficiency (l/W)	Efficiency (W/W) %	Life to 50% of Initial Brightness; Coulomb/cm ²
P-1	30	5.7	100
P-4	40	14	25
P-7	20	8.7	25
P-11	22	15	25
P-16	0.09	3.7	0.1
P-20	65	13.5	25
P-22B	17	11.5	30
P-22G	65	13	20
P-22R	7.5	2.7	45
P-24			9
P-26	10	2.4	0.05
P-31	50	11.7	30
P-33	14	3.2	0.05
P-39	22	4.3	100
P-43	40	9.6	80
P-44	30	5.5	50
P-45	22	7.6	50
P-46	13	2.5	100
P-47	2.3	3.2	50
P-53	30	4.5	100

Table 3. Phosphor Parameters and Applications

Type	Color	Spectral Peak (Angstroms)	Kelly Chart Coordinates		Persistence	Decay to 10% Brightness	Applications
			X	Y			
P1	Yellowish Green	8250	.218	.712	Medium	24msec	General Purpose Visual Displays
P2	Yellowish Green	8350	.279	.534	Med. Short	~75µsec	Largely Superseded by P31
P3	White	4600 8600	.270	.300	Med. Short	20µsec 60µsec	60Hz Television
P7	Blue Yellow Green	4400 5550	.151 .357	.032 .537	Med. Short Long	~50µsec .35sec	Radar and Oscillography
P11	Blue	4600	.139	.148	Med. Short	~50µsec	Photographic Recording
P12	Orange	5900	.605	.394	Long	200msec	Low Frame Rate Displays & Radar
P14	Purplish Blue Yellowish Orange	4400 6000	.150 .504	.093 .443	Med. Short Medium	25µsec 8msec	Radar
P16	Bluish Purple	3800	.175	.003	Very Short	.12µsec	Flying Spot Scanners & UV Recording
P18	Orange	8900	.572	.442	Long	220msec	Radar
P20	Yellow Green	5600	.426	.546	Med. Short	~.2µsec	Bright Visual Displays
P24	Green	5100	.245	.441	Short	~1.5µsec	Color Flying Spot Scanner
P26	Orange	6100	.857	.430	Medium	45µsec	Radar
P28	Orange	8950	.882	.416	Very Long	~10sec	Radar

Table 5. (cont.).

Type	Color	Spectral Peak (Angstroms)	Kelly Chart Coordinates X Y	Persistence	Decay to 10% Brightness	Applications
P28	Yellow Green	8600	.370 .840	Long	~.5sec	Long Persistence at Low Brightness Only
P31	Green	8200	.193 .420	Med. Short	40μsec	Bright Visual Displays Oscillography
P33	Orange	5875	.559 .440	Very Long	~10sec	Radar
P36	Yellow Green	8500	.400 .543	Very Short	.25μsec	Flying Spot Scanners
P37	Blue	4700	.143 .206	Very Short	.15μsec	Flying Spot Scanners & Photographic Recording
P38	Orange	6000	.561 .437	Very Long	fsec	Low Frame Rate Displays & Radar
P39	Yellowish Green	8250	.223 .698	Long	150msec	Medium Frame Rate Displays & Radar
P40	White	4400	.276 .311	Med. Short	150μsec	Longer Persistence Vision of P4
	Yellow Green	8500		Long	~.5sec	
P41	Greenish Yellow	8900	.541 .456	Long	20μmsec	Low Frame Rate Display with Light Pen
		3800	.175 .003	Very Short	.12μsec	
P42	Yellowish Green	8200	.238 .568	Med. Long	10msec	Medium Frame Rate Display
P43	Yellowish Green	5440	.333 .556	Medium	1.2msec	Bright High Contrast Dis- plays with Band Pass Filter

Table 5. (cont.).

Type	Color	Spectral Peak (Angstroms)	Kelly Chart Coordinates X Y	Persistence	Decay to 10% Brightness	Applications
P44	Yellowish Green	5440	.300 .896	Medium	1.2msec	Bright High Contrast Displays with Band Pass Filter
P45	White	.	.253 .312	Medium	1.7msec	Preferred Alternative to P4 for High Brightness White Displays
P46	Yellow Green	8300	.365 .895	Very Short	0.16µsec	Flying Spot Scanners, Preferred Alternative to P36
P47	Purplish Blue	4000	.166 .101	Very Short	.080µsec	Flying Spot Scanners, Superior to P16 in Most Applications
P48	Yellow Green	4000	.365 .474	Very Short	0.12µsec	Color Flying Spot Scanner Superior to P24 in Most Applications
P49	Red 10KV Green 17KV	6150 8150	.472 .327 .3115 .615	Medium Medium	1.2msec 30msec	High Resolution Multi Color
P50	Red 8KV Yel. Green 15KV	6200 8450	.655 .340 .398 .546	Medium Med. Short	5msec 30µsec	High Resolution Multi Color
P51	Red 6KV Yel. Green 12KV	6225 5450	.675 .325 .414 .614	Medium Med. Short	2.2msec 31µsec	High Resolution Multi Color
P52	Purplish-Blue	4000	.157 .075	Med. Short	26µsec	Photo Recording

Multiple Peaks.

band structure investigation. Among the relatively new phosphors, $\text{SnO}_2:\text{Eu}$ presents a certain interest not only because of its luminescence parameters, but also because of its secondary electron emission properties and transparency in the visible part of spectrum [20, 21].

Another interesting compound, from our point of view, is a wurtzite type crystal LiInS_2 [22] that belongs to the I-III-VI₂ group and may be as effective a material for deep-blue-light emitting devices as ZnS [23], ZnSe [24, 25], GaN [26], etc. The origin of the blue-light emission in these materials is attributed to the intrinsic anion vacancies. The emission properties of the other known representative of the group, LiCaO_2 [27] are waiting to be investigated.

4.1. On the Phosphor Degradation

There have been several possible models offered for explanation of the cathodoluminophor deterioration, especially in fluorescent lamps, namely, (a) absorption of ions (mercury, in particular) by the phosphor particle surface [30-34]; (b) formation of color centers by the UV radiation [35-39]; (c) structural changes in the phosphor material caused by exposure to ion bombardment [29, 34, 40, 41]; (d) oxidation or reduction of activator ions, or of the phosphor matrix, to a nonluminescent state by action of UV quanta [42, 43]; (e) some dependence of phosphor deterioration on the kind of substrate under it and diffusion of the substrate ions into the phosphor. As mentioned in [28], this possibility cannot be completely ignored and might warrant further investigation, but with our present knowledge, there is no reason to expect it to be a major cause of phosphor deterioration.

As was shown by Lehman [28] and Tada et al. [29], the main cause of the CL deterioration is physical damage of its surface. The ion bombardment builds up a disordered and nonluminescent layer on the phosphor particles. Such layers have been observed on several CLs. This model explains the experimentally observed time dependence of brightness.

$$B(t) = B(0)\exp[-(t/\tau)^{1/2}] \quad (5)$$

where $B(t)$ and $B(0)$ are brightness at the moment t and at the moment 0, and τ is a constant denoting the time necessary to decrease brightness to $\exp(-1) = 0.37$ of

the initial magnitude. The thickness of the amorphous non-luminescent layer varies from 5-10A on a non-aged CL to 3000A as observed on zinc silicate in [29] after the 200 eV Ar^+ ions' bombardment. Damage of phosphors by He^{2+} ions and by H_2^+ ions was investigated in [44] and [45] respectively. The general observation [46-48] is that, in the process of bombardment, the crystallophosphor atoms are displaced from their positions to more or less irregular sites, and this amorphous state destroys luminescence.

It deserves to be noted that the amorphous layer has an optical absorption on its own. This means that it not only excludes itself from the radiation generation, but also absorbs a part of the luminescence of the undamaged single-crystalline grains.

4.2 Conclusion

In spite of existence of the vast amount of publications relevant to chemistry and physics of cathodophosphors, many of the questions regarding their efficiency, spectral composition, choice of optimal activators and coactivators, decay and deterioration characteristics, their performance characteristic in some devices, particularly in the image intensifiers are far from being exhaustively answered. There are some publications in which only a few phosphors were investigated as part of intensifiers (UC Berkeley, University of Arizona, Tucson). The role and behavior of the residual ions in the electric field of a cathode-ray tube, interaction of the phosphor with the electrode material, physicochemical processes in the bulk and on the surface of a phosphor grain and their relations to the phosphor efficiency and degradation are subjects of a less than complete list of the problems that have to be solved to make the process of choice of a phosphor for a certain application more purposeful and expedient.

5. Cathodophosphors: Developmental Work

5.1. IIB-VIB Phosphors

The latest developmental work with IIB-VIB phosphors is directed toward understanding the role of the isoelectronic additives in the cathodoluminescence (CL) of CdS and ZnS and investigation of correlation between the heat treatment parameters and CL of some of the compounds.

It is known (see, e.g., Ref. [51-54]), that the isoelectronic substitutional atoms form the effective radiative recombination centers in some semiconductor compounds if their ion radius and electro-negativity differ substantially from those of the replaced atoms. Such behavior of the tellurium atoms in ZnS and CdS was described in [51-53], of the oxygen atoms in ZnTe in [53], and of the nitrogen atoms in GaP in [54]. The quantum efficiency of such a recombination at low isoelectronic impurity concentration ($< 10^{20} \text{ cm}^{-3}$) and low excitation rate is close to unity [51]. This property of the isoelectronic recombination centers can be used in the fabrication of LED's and electroluminescent screens [55, 56], of scintillators [57], and apparently, for fabrication of high quantum efficiency CRT screens. An investigation of the cathodoluminescence associated with the Te additive in $\text{CdS}_{1-x}\text{Te}_x$ and $\text{ZnS}_{1-x}\text{Te}_x$ ($x = 10^{-5}$, 10^{-3} , and 2×10^{-2}) at high excitation rates [58] showed that at higher concentrations of Te ($> 10^{19} \text{ cm}^{-3}$) the cathodoluminescence spectrum consisted only of the lines associated with tellurium. A study of the quantum efficiency, η , as a function of the current density, J , and the Te content showed that η does not depend on J until it reaches a saturation magnitude J_s after which η decreases very fast. For crystals $\text{CdS}_{0.98}\text{Te}_{0.02}$ and $\text{ZnS}_{0.98}\text{Te}_{0.02}$ at the electron energy 75keV, J_s is equal to about $1 \mu\text{A}/\text{cm}^2$ and $10 \mu\text{A}/\text{cm}^2$, respectively. These results in combination with the fact that the "edge luminescence" of the materials ($\lambda = 520 \text{ nm}$ and $\lambda = 350 \text{ nm}$ for CdS:Te and ZnS:Te, respectively) may be considered as proof of the effective use of the II-VI diluted solid solutions for the CRT screens.

Cathodoluminescent properties of undoped ZnSe epilayers was reported in [59, 60]. The initial material had superstoichiometric Se. The layers were annealed under the evaporation conditions to eliminate the zinc

vacancies. The most intensive band in the edge CL spectrum was a doublet structure due to free excitons. The experiments showed that annealing ZnSe:Se crystals not only eliminates superstoichiometric selenium but also certain residual uncontrolled impurities (in particular, lithium atoms).

The results of [60] are in some contradiction with reports [61, 62] where the authors concluded that annealing in vacuum produced the same effect on the radiative properties of ZnSe as annealing in selenium. This conclusion is the consequence of the choice of the annealing technique. The authors of [63], who annealed the ZnSe crystals in vacuum 10^{-6} torr, showed that the results of annealing are different depending on the details of process (e.g., on rate of cooling the ampoule with the crystal after annealing period is over, etc.), as can be seen from the CL spectra.

5.2. IIA-VIB Phosphors

As was mentioned in [64], IIA-VIB compounds and solid solutions on their basis are known as excellent and versatile phosphor hosts. Using different activators and coactivators produces phosphors that emit colors from the deep red to near ultraviolet [65-69]. CaS:Ce^{3+} has been known as an excellent green emitting phosphor [66]. Its CL efficiency and color parameters are comparable to those of the best green-emitting IIB-VIB phosphors. This phosphor shows also much less brightness saturation at high beam currents [66].

Another IIA-VIB phosphor of current interest is SrS:Ce^{3+} with peak position of CL at 483 nm and color coordinates (0.198; 0.435). The solid solutions in the system CaS-SrS [64] can be used to make a CL phosphor with the peak position from 508 to 483 nm which is a linear function of x in $\text{Ca}_x\text{Sr}_{1-x}\text{S:Ce}_{0.001}$ and with the energy efficiency comparable with that of the $(\text{Zn,Cd})\text{S:Cu,Al}$ phosphor being measured at 8kV and current density from 0.1 to 10 $\mu\text{A}/\text{cm}^2$.

For terminal display tubes, an orange-emitting phosphor of composition $(\text{Ca}_{0.985}\text{Mg}_{0.015})\text{S:Mn}_{0.008}$ was developed [70] to replace the environmentally hazardous halophosphate $\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2\text{Mn}$. The work in the field of alkali-halide chalcogenide phosphors is apparently on the rise; so far there is only one standard (USA)

phosphor, namely P-32, that contains these materials. Although mentioned earlier, a big family of alkaline earth chalcogenide phosphors has been known since the early part of this century [71].

5.3. Silicates, Borates, Carbonates, Phosphates, and Tungstates (Wolframates)

This group of phosphors is one of the most widely used in the industry of the luminescent sources of radiation. Zn_2SiO_4 is the only component of the yellowish green (YG) P-1 phosphor (activated by Mn), the (YG) P-39 phosphor (with Mn and As), and the purplish blue P-52 phosphor (with Ti). It is a part of the green P-22G phosphor ($\text{Zn}_2\text{SiO}_4:\text{Mn} + \text{ZnCdS}:\text{Cu,Al,Au}$), the multicolor P-49 phosphor ($\text{Zn}_2\text{SiO}_4 + \text{YVO}_4$), and the P-57 phosphor ($\text{Zn}_2\text{SiO}_4:\text{Mn} + \text{KMgF}_3:\text{Mn}$). A standardized orange P-25 phosphor ($\text{CaSiO}_3:\text{Pb,Mn}$) used for radars and purplish blue P-47 phosphor ($\text{Y}_2\text{SiO}_5:\text{Ce}$) are the other silicates that may be considered of interest for investigation, especially the latter one which has spectral peak at 400 nm and decays to 10% brightness in 80 ns.

Among borates, the orange phosphor $\text{InBO}_3:\text{Eu,Tb}$ [72] deserves to be mentioned. It is chemically stable, has the persistence of 20 ms, and its brightness is comparable with that of a standard white phosphor P-54 and some other high brightness phosphors.

In the literature, there are data on the thermal luminescence of CaCO_3 activated by Mn^{2+} , Cu^{2+} , or Pb^{2+} [73]. Another carbonate of interest is SrCO_3 , with the crystal structure of the aragonite type [74]. Strontium carbonate presents a specific interest because of its ability to produce self-activated luminescence in the region 490 nm [75]. This luminescence is most probably produced by the CO_2^- radicals in the interstitials of the SrCO_3 aragonate lattice. The cathodoluminescence properties of SrCO_3 certainly may present a practical interest as they may be controlled by a combined action of activating impurities and self-activators.

Among phosphates used in the standard CL are $\text{Zn}_3(\text{PO}_4)_2:\text{Mn}$ which is used in combination with $\text{YVO}_4:\text{Eu}$, $\text{Y}_2\text{O}_3:\text{Eu}$, and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ as a red part of the P-22 phosphor in color TV, and as the only ingredient of the reddish-orange P-27 (RE) phosphor $\text{Zn}_3(\text{PO}_4)_2:\text{Mn}$ that is used in color TV monitor service.

The only tungstate that has found practical use is the blue P5 (BJ) phosphor $\text{CaWO}_4:\text{W}$, color parameters $X = 0.169$, $Y = 0.132$, the 10% decay time 25.5 μs . This material is still in the process of investigation. Its main physico-chemical properties such as phase equilibria, solubility of optical active impurities, etc., are not known.

5.4. Garnets

The garnets, of which the best known is $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), are widely used and studied as host lattice, e.g. for laser materials, and magneto-optical storage materials [76-79]. Activated with suitable ions, they are excellent phosphors [80-85]. There are two standard phosphors on the basis of YAG, namely P-46 (KG) with Ce^{3+} and P-48 (KM) with Tb^{3+} as an activator. Both produce yellow-green radiation but the former has τ (10%) = 160 ns, whereas the latter has τ (10%) = 7 ms. An improved P-53 phosphor is a solid solution of YAG and yttrium gallium garnet $\text{Y}_3\text{Ga}_5\text{O}_{12}$ activated by Tb^{3+} . Another fast standard phosphor is the white GU which is a mixture of YAG:Ce and yttrium silicate: Ce. Its CL spectrum has two broad peaks at 420 and 520 nm.

Garnets now are in the focus of attention of the CL materials specialists, particularly because some of the garnets (e.g., $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Tb}$) are excellent X-ray phosphors [86]. One of the most important questions now is whether the powder or single crystal is better for use in the CL devices. Undoubtedly, technology of deposition of the powder phosphor on the faceplate of CRT tubes is less expensive than that of the epitaxial (or polycrystalline) layer, but grain structure of the phosphor screen is fraught with the possibility of the total internal reflection and consequent absorption of the radiation inside of a grain in which the radiation was produced. From the experimental data (see, e.g., [87-90]), at least part of the irradiated photon losses may be explained by this effect.

The single-crystalline YAG phosphor [91] has definite advantages due to the lack of optical scattering within the phosphor, the superior lifetime of the monocrystal phosphor due to the absence of coulombic degradation, and high thermal conductivity of the crystal in comparison with the multigrain layers. Comparison of the results of current investigation of powder [92] and

single crystalline [93] YAG phosphors in the same laboratory (AT&T Bell Labs., Murray Hill) shows that the LPE growth of YAG phosphors activated by Ce, or Tb, or both, permits the material to have efficiency up to 11% which is, about three times that for the standard powder phosphor P-47.

The choice of activator(s) and its contents substantially change the peak wavelength of YAG and the time characteristics as was shown in [94] on the phosphors YAG:Er³⁺, Yb³⁺, and in [95] where CL efficiency of YAG and YAlO₃ single crystals with different amounts of Ce, Nd, I₂, Fe, Ti, and Cr dopants had been studied. Nevertheless, YAG, as well as YAlO₃ and MgAl₂O₄ spinel, exhibit intensive intrinsic CL especially at low temperatures (see, e.g. [46]).

The Tb-activated YAG which CL properties were briefly discussed in this report, shows little tendency to saturate at high current excitations and is fairly insensitive to temperature variation [97]. There is another way to increase the saturation brightness of YAG by replacing a portion of aluminum with gallium as was reported in [98]. The results of a thorough investigation of crystal structure and CL properties of Y₃Al_{5-x}Ga_xO₁₂:Tb (0 < x < 5), namely, relative brightness, its temperature and current density dependence, CL spectra and the focusing voltage dependence of brightness as the function of composition of YGaG are presented in [99]. At high cathode currents, brightness of a YGaG:Tb is about twice greater than that of YAG:Tb. From our point of view, the detailed investigation of solid solutions on the YAG basis may reveal new prospective combinations of the CL properties.

5.5. II-VI/III-VI Phosphors with the Stoichiometric Defects

Investigation of these phases is a continuation of study of II-VI phosphors. As long ago as 1963, the II-III-VI compounds were investigated as luminescent materials. Luminescence of CdGa₂S₄ and CdIn₂S₄ was reported in [100]. Room temperature luminescence of ZnIn₂S₄:Cu had been studied in [101]. From our point of view, a prospective for CL materials of this type is HgIn₂S₄ with E_g = 2.79 eV (see, e.g. [102-104] for the blue CL. A detailed study of the CdGa₂S₄ CL has been done by authors of [105]. At room temperature this material

shows blue-light blue CL which is attributable to a deviation from stoichiometry, namely, to centers associated with excess cadmium in the specimens.

Another developmental work of interest is investigation of solid solutions of the binary defect III-VI compounds. In [106], the results of the CL measurements of the solid solutions $\text{Ga}_2(\text{S}_x\text{Te}_{1-x})$ showed an intense and stable orange CL emission of $\text{Ga}_2(\text{S}_{0.73}\text{Te}_{0.27})_3$ at room temperature at electron energy 25 keV and current 10 nA. Unfortunately, this work cannot be considered as a convincing one because the X-ray analysis of the specimens showed presence of two phases in them. Optical properties of some individual A_2B_3 defect compounds are described in [107, 108].

6. Photoluminescent Materials

Although this project is devoted to analysis of data relevant to CRT materials, a brief consideration of the photoluminescence materials may open new opportunities in search for most appropriate CL's for some particular applications.

6.1 Rare Earth Silicates, Phosphates, etc.

The luminescence properties of rare earth oxyorthosilicates $\text{Ln}_2(\text{SiO}_4)_2\text{O}$ ($\text{Ln} = \text{La, Gd, Y}$) activated with suitable activators have studied extensively [109-115]. The luminescence of these phosphors is very efficient both under cathode-ray and optical excitation. The latest available results [116] showed that the best phosphor of this group is $\text{Gd}_2\text{SiO}_5:\text{Tb}^{3+}$ both under UV and X-ray excitation.

Another interesting and relatively new group of phosphors is the material based on sensitized rare earth ion sublattice. The first phosphors of this type were based on a sensitized Gd^{3+} sublattice [117]. The excitation energy migrates over this sublattice to a built-in activator (for example, Tb^{3+}). The search for a more efficient phosphor of this type is on the rise [118, 119]. Following investigations on rare earth trifluorides [120, 121] and $\text{Li}(\text{Y,Gd})\text{F}_4:\text{Ce,Tb}$ [122], the authors

of [123] investigated the luminescent system $\text{NaY}_{1-x-y-z}\text{Gd}_x\text{Ce}_y\text{Tb}_z\text{F}_4$ ($x = 0.05, 0.95, 0.989$; $y = 0.01, 0.04$; $z = 0.001, 0.01$). They found quite high quantum efficiency of luminescence at room temperature (over 90%), but a drawback is a relatively long afterglow.

A detailed investigation of luminescence of the quasi-binary tetrafluorides $(1-x)\text{BaMgF}_4-(x)\text{EuMgF}_4$ was undertaken by the authors of [124]. The intensity of luminescence in the phase $\text{Eu}_x\text{Ba}_{1-x}\text{MgF}_4$ increases with x and reaches a maximum at $x = 0.4$. It is interesting to mention that the similar concentration dependence of the emission intensity was described in [126] for the $\text{Gd}_{3-x}\text{Tb}_x\text{Ga}_5\text{O}_{12}$. The authors of [126] found that the intensity curve passes through a maximum at $x = 0.18$. A similar dependence of intensity on concentration was described in [126] for $\text{Y}_{3-x}\text{Tb}_x\text{Al}_5\text{O}_{12}$. Apparently, it is typical for the true solid solutions. The peak of the emission spectrum shifts to the longer wavelength with the x increase. Some results of [124] are presented in Table 6.

Table 6. Some Spectral Data of $\text{Eu}_x\text{Ba}_{1-x}\text{MgF}_4$ [124]

x	0.02	0.05	0.10	0.15	0.30	0.40	0.50	0.60
Emission peak (nm)	415	416	418	419	422	--	--	426
Stokes shift (eV)	1.07	1.02	0.90	0.74	0.66	--	--	0.63
Luminescence intensity (a.u.)	-2	-18	-40	-60	-83	-90	-80	-70

The authors of [125] have observed that the Eu^{2+} luminescence in the $\text{Ba}_{1-x}\text{Eu}_x\text{MgF}_4$ can be greatly affected if there exists contamination by oxide ions in the crystal lattice of the tetrafluoride. The emission band of $\text{Ba}_{1-x}\text{Eu}_x\text{MgF}_4$ is quite wide; its half-width for a $\text{Ba}_{0.60}\text{Eu}_{0.40}\text{MgF}_4$ is close to 0.3 eV at room temperature.

Unfortunately, there are no reliable published data regarding the luminescence decay time in these solid solutions.

7. The Low Energy Electron Cathodophosphors

One of the most important difficulties in development of effective phosphors for CRT's is appearance of the strong negative charge on the side of the screen looking at the electron source. The common means to eliminate this charge is allumination of this side and acceptance of the loss of part of electrons that otherwise would penetrate into the phosphor and produce the CL. This charge is also partially responsible for usually high threshold voltage for emission.

The first material that was successfully used for low-energy electron (LEE) devices was ZnO:Zn [127-129] and CdS:Ag [130]. A large group of new LEE excitation phosphors in addition to the bluish-green ZnO:Zn have been since developed [131-135]. Promising results were reported in [136, 141] regarding LEE emission of the SnO₂:Eu powders. This material was investigated in the crystalline form by Crabtree [137-140], but the relatively high efficiency of 2 lm/W was obtained on the powder CL [141].

A large group of LEE excitation CL materials was investigated by authors of [142], including ZnO:Zn, the mixtures Y₂O₂S:Eu + In₂O₃, ZnS:Cu,Al + In₂O₃, ZnS:Cu,Al + SnCl₄, the solid solutions (La_xLu_{1-x})InO₃:Eu, and the oxysulfide luminophor LaInO₂S:Eu. The ZnO:Zn brightness reached 1000 ft-L when applied voltage increased from 5-15V (threshold) to 25-50V depending on the cathode-anode distance. The brightness of the mixture Y₂O₂S + In₂O₃ is a function of both diameter of the Y₂O₂S:Eu particles and In₂O₃ contents. At d = 10 μm, 25% In₂O₃ and V = 90V, brightness exceeds 250 ft-L. The solid solution (La_xLu_{1-x})InO₃:Eu phosphor has a sharp rise of the emission intensity with the x increase. The material with highest brightness has x = 0.75. The solid solutions emit CL radiation with the strongest band between 810 and 830 nm.

8. Conclusion

1. The rare-earth ion activated high resistance phosphors based on the materials with garnet, spinel and diamond structure can be considered as the most prospective CL materials, especially in the compounds that include the rare-earth elements in their host matrix.
2. The low resistance CL oxides, being either components of a CL phosphor mixture or a part of its matrix, may be considered as one of the most prospective objects of investigation in the search for CL phosphors with the improved characteristic parameters.
3. The developmental work in this field has to be directed toward investigation of a way to improve the phosphor quantum efficiency and solution of the lost electron problem.
4. The role and behavior of the residual ions in the electric field of a CRT, interaction of the phosphor with the electrode material, physicochemical processes bulk and on the surface of the individual phosphor grains have to be the topics of development work in the field of CL materials.

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Appendix

Basic Characteristics of Some
Commercially Available Cathodophosphors

40

Designation AA

Alternate or obsolete designation Pl6

Registration Date 5-16-55 Registrant RCA

Color #1 Name Violet UV

X: 0.199 Y: 0.016 U': 0.285 V': 0.052

Color #2 Name _____

X: _____ Y: _____ U': _____ V': _____

Color #3 Name _____

X: _____ Y: _____ U': _____ V': _____

Composition Phosphor #1 Calcium magnesium silicate: cerium

Composition Phosphor #2 _____

Composition Phosphor #3 _____

Persistence (to 10% ILR)

Phosphor #1 _____ Phosphor #2 _____ Phosphor #3 _____

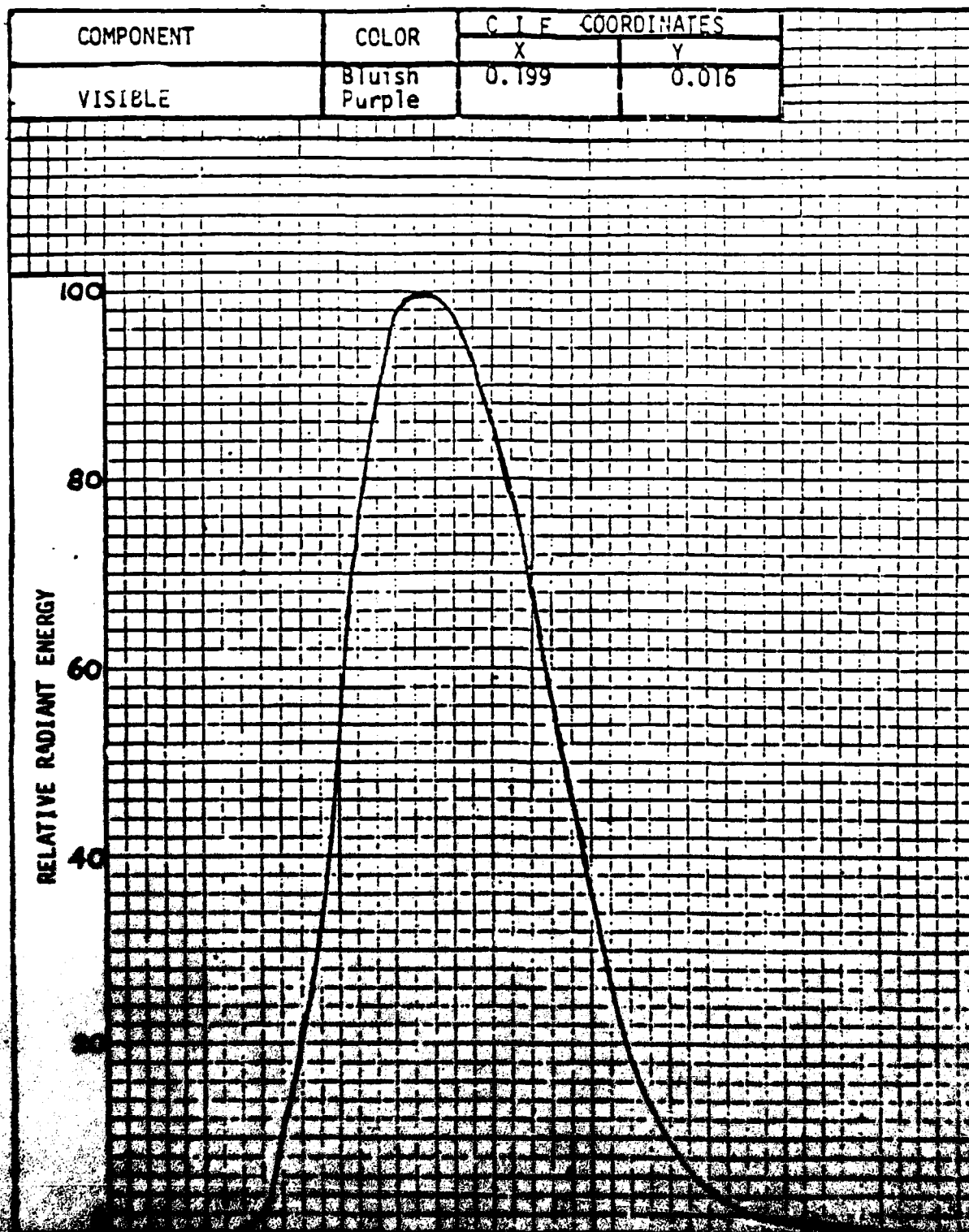
Persistence Method: _____

Persistence Conditions:

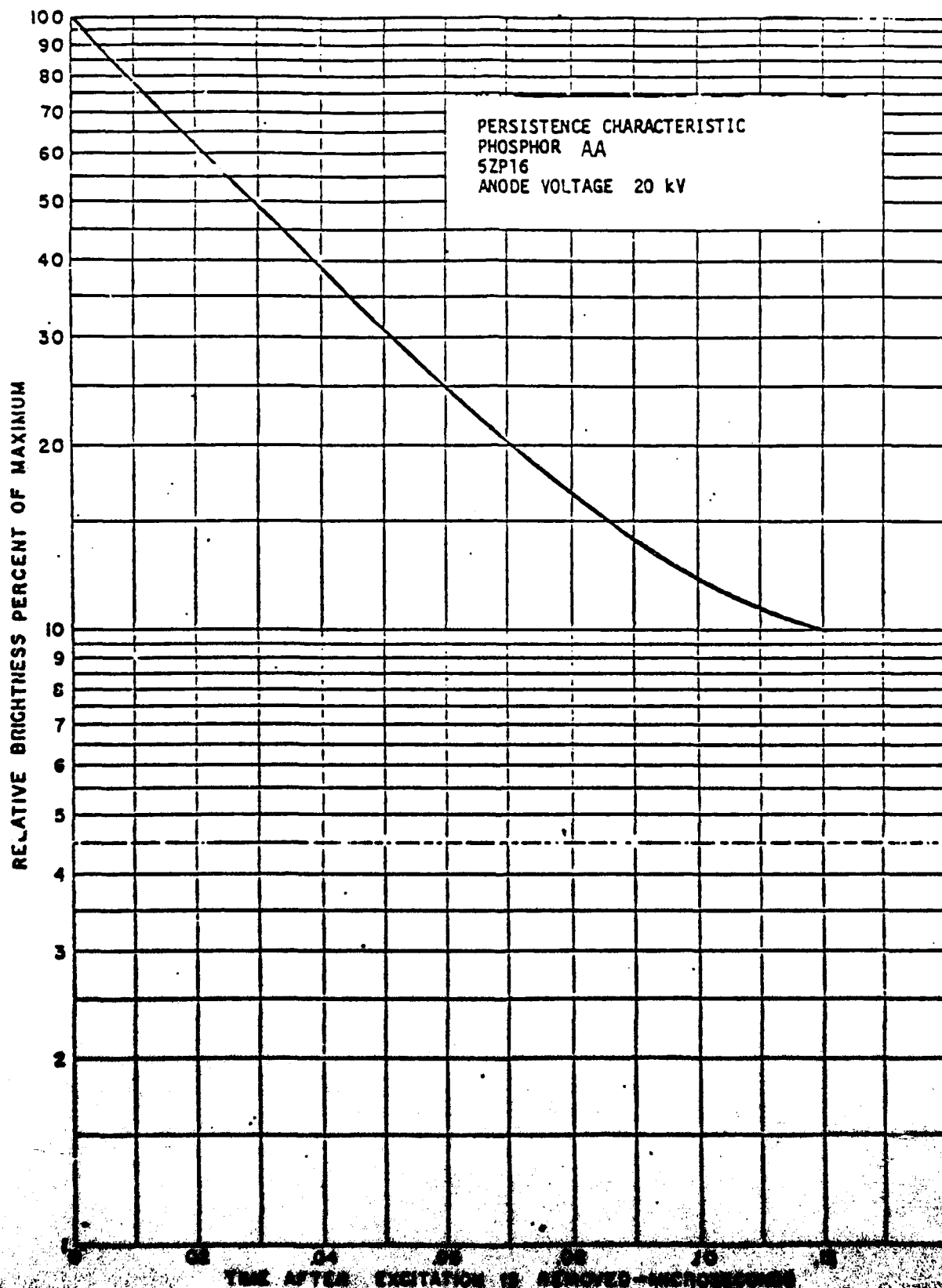
Comments:

	100	50	20	10	5	2	1
time	0	.03	.07	.12	microseconds		

SPECTRAL-ENERGY DISTRIBUTION CHARACTERISTICS
OF PHOSPHOR TYPE AA



42



43

Designation BA

Alternate or obsolete designation -

Registration Date - Registrant Philips

Color #1 Name Purplish Blue Fluorescence
X: .164 Y: .015 U': .230 V': .047

Color #2 Name _____
X: _____ Y: _____ U': _____ V': _____

Color #3 Name _____
X: _____ Y: _____ U': _____ V': _____

Composition Phosphor #1 _____

Composition Phosphor #2 _____

Composition Phosphor #3 _____

Persistence (to 10% ILR)

Phosphor #1 _____ Phosphor #2 _____ Phosphor #3 _____

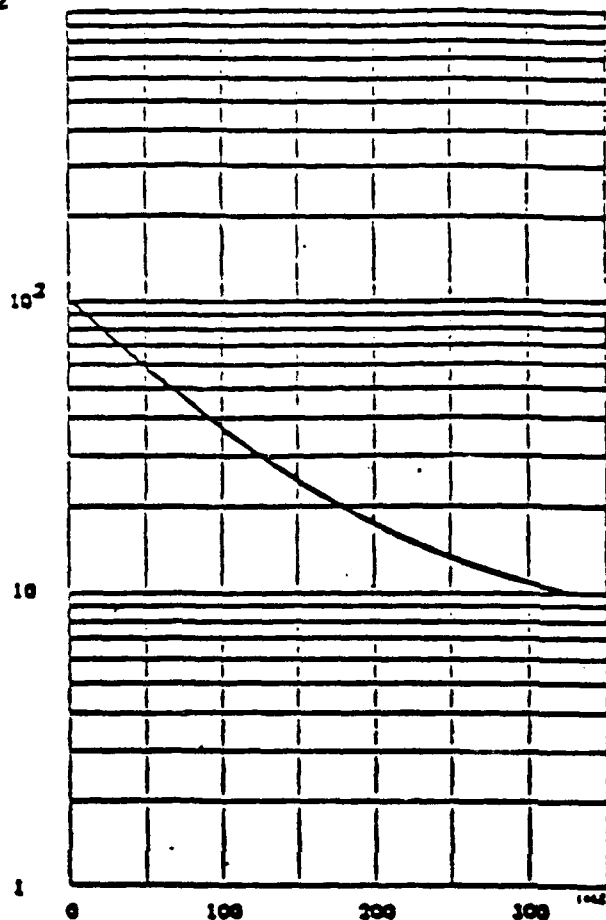
Persistence Method: _____

Persistence Conditions:

Comments:

Percent	100	50	20	10
Milli-microseconds	0	70	180	

Percentage of initial light output



Time from cessation
of excitation (msec.)

Phosphor screen designation

BA

Colour

fluoresc. phosph. ICI coord.

purplish

$x = 0.164$

blue

$y = 0.015$

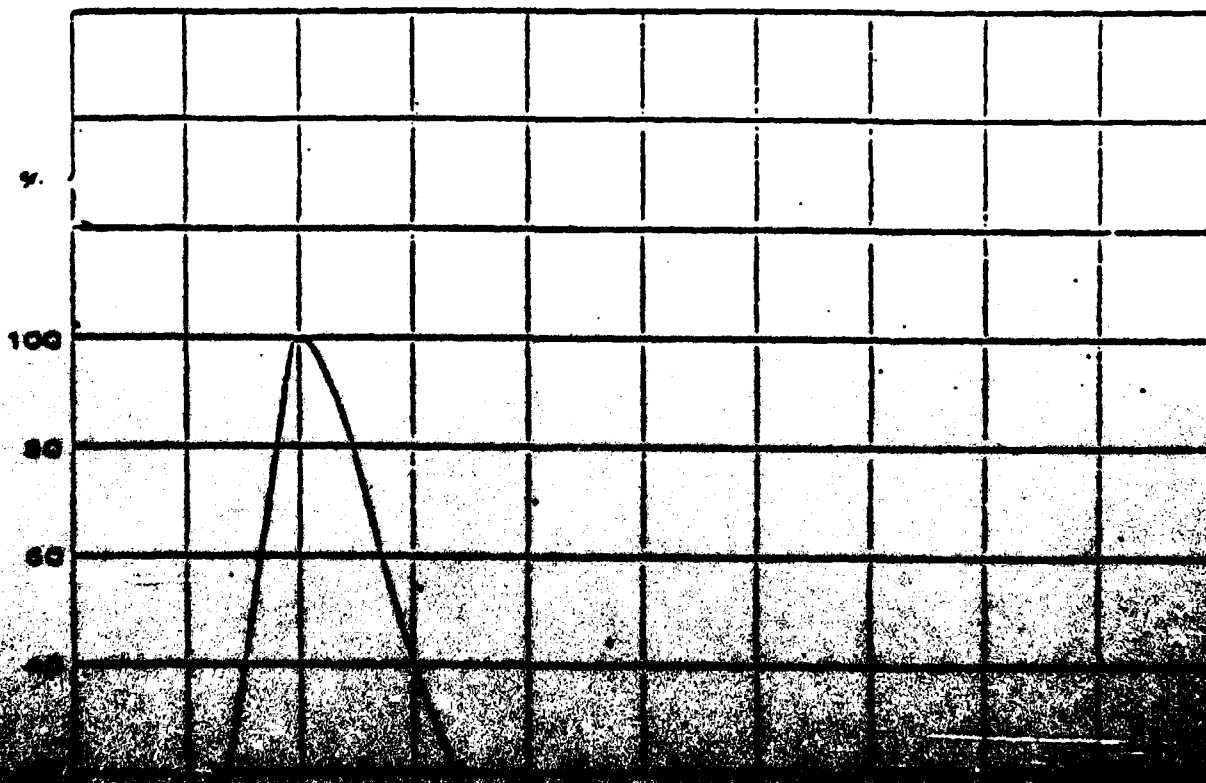
Persistence (%)

very short (1/e after 100 msec.)

Conditions for persistence measurement

In flying spot scanner applications the persistence is independent of curvet density and excitation time.

Relative spectral energy distribution



45

Designation BC

Alternate or obsolete designation -

Registration Date 1962 Registrant Mullard

Color #1 Name Violet Fluoresc.

X: .170 Y: .024 U': .231 V': .073

Color #2 Name

X: Y: U': V':

Color #3 Name

X: Y: U': V':

Composition Phosphor #1 Zinc sulfide; silver, Aluminium

Composition Phosphor #2

Composition Phosphor #3

Persistence (to 10% ILR)

Phosphor #1 Short Phosphor #2 Phosphor #3

Persistence Method:

Persistence Conditions:

Comments:

[illegible]

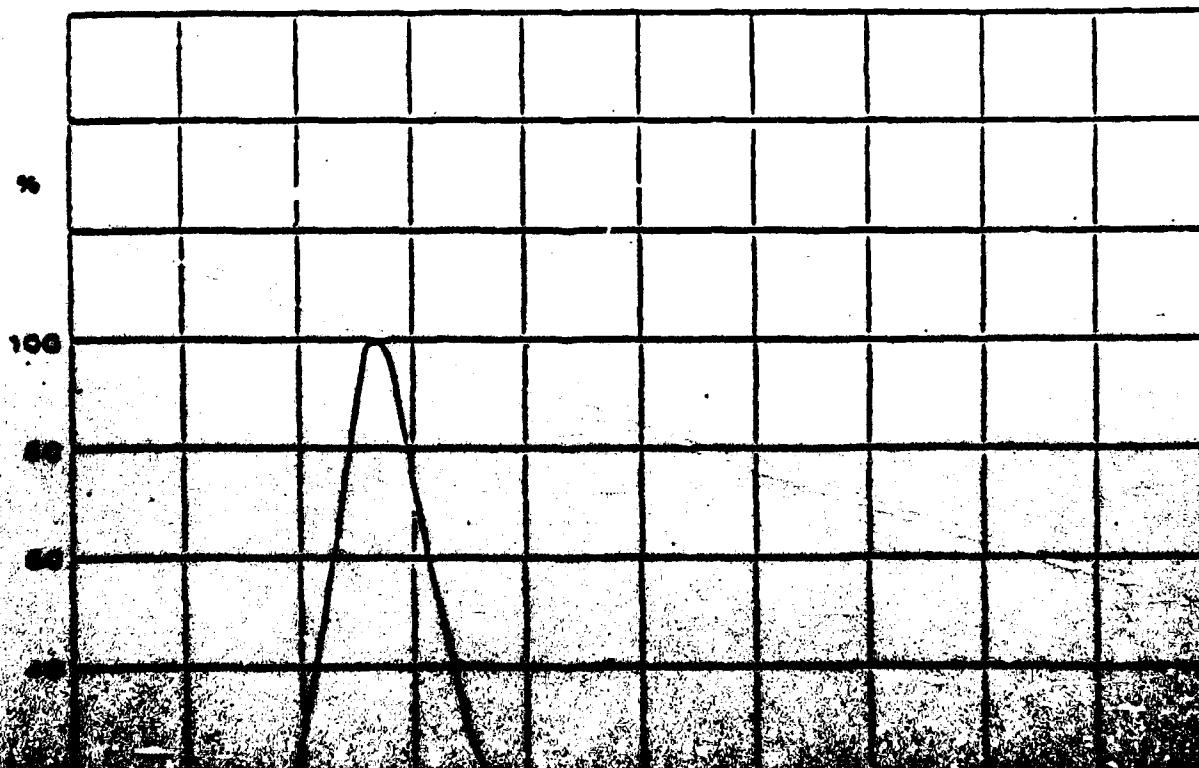
BC

fluoresc phosph LCI coord
violet $x = 0.170$
 $y = 0.074$

short

Conditions for persistence measurement

REPORTING PERIOD: ALL:200 PERIODS: 0000000000



47

Designation BD

Alternate or obsolete designation -

Registration Date 1962 Registrant Mullard

Color #1 Name Blue Fluoresc.

X: .198 Y: .220 U': .151 V': .378

Color #2 Name

X: Y: U': V':

Color #3 Name

X: Y: U': V':

Composition Phosphor #1 Zinc sulfide: silver, Nickel

Composition Phosphor #2

Composition Phosphor #3

Persistence (to 10% ILR)

Phosphor #1 Very Short Phosphor #2 Phosphor #3

Persistence Method:

Persistence Conditions:

Comments:

[illegible]

BD

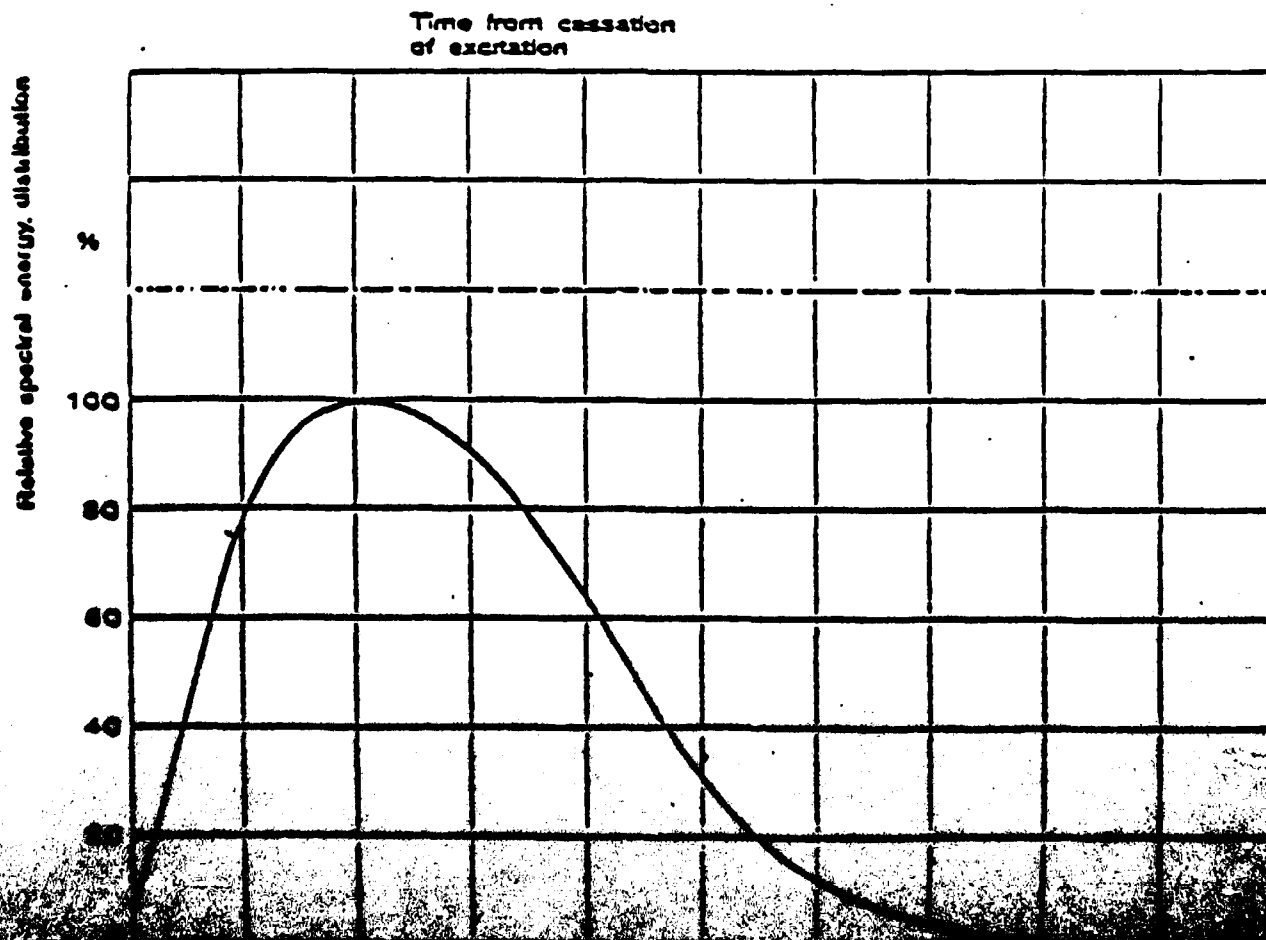
fluoresc phosphor LCL cord

2002:98

7 - 0220

very short (1/2 after 100 msec.)

Conditions for persistence measurement



49

Designation BH
 Alternate or obsolete designation P47
 Registration Date 7-17-72 7-20-77 Registrant Thomas M-O Valve Co.

Color #1 Name Purplish Blue
 X: .166 Y: .101 U': .171 V': .234

Color #2 Name _____
 X: _____ Y: _____ U': _____ V': _____

Color #3 Name _____
 X: _____ Y: _____ U': _____ V': _____

Composition Phosphor #1 Yttrium silicate: cerium

Composition Phosphor #2 _____

Composition Phosphor #3 _____

Persistence (to 10% ILR)

Phosphor #1 _____ Phosphor #2 _____ Phosphor #3 _____

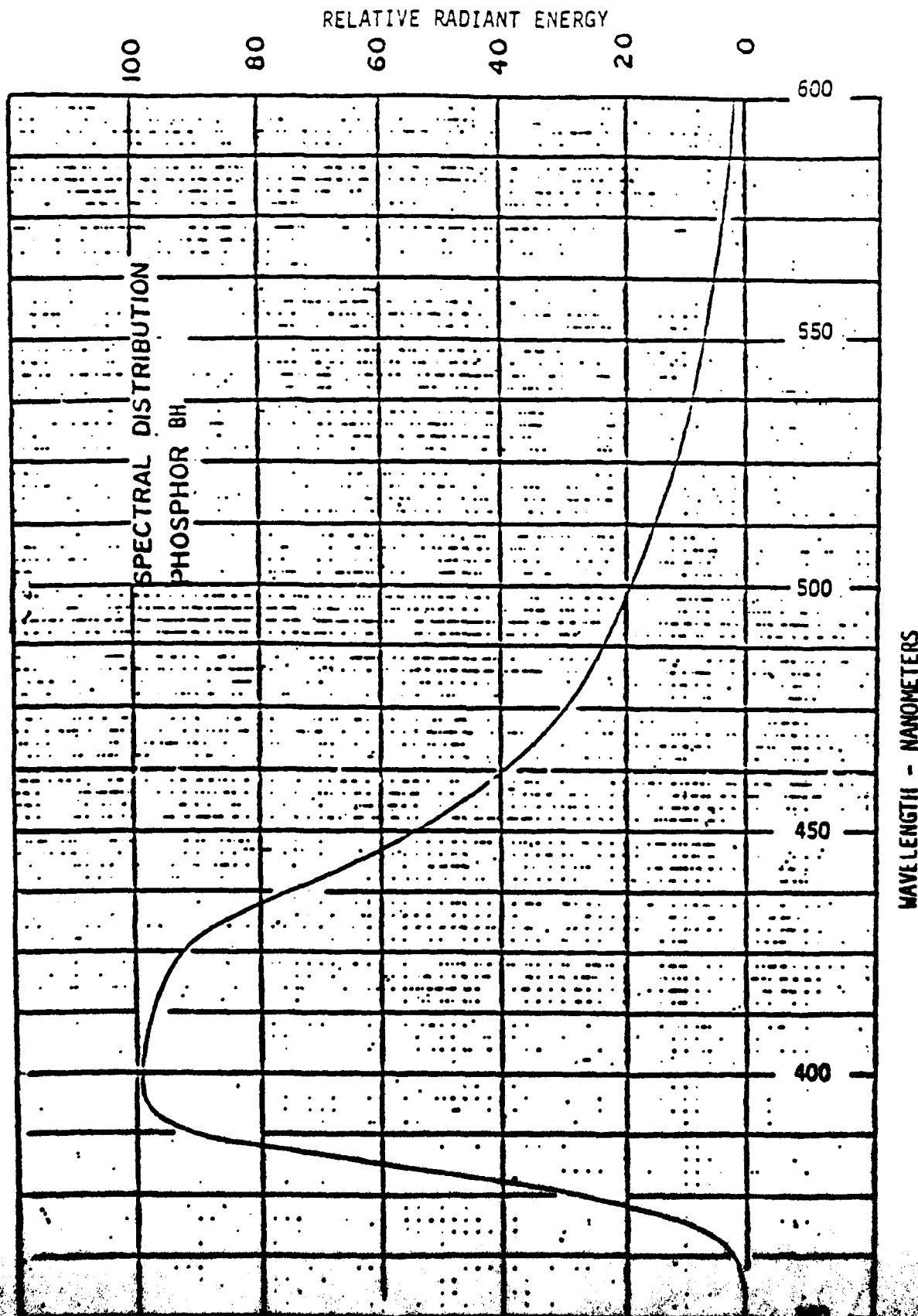
Persistence Method: _____

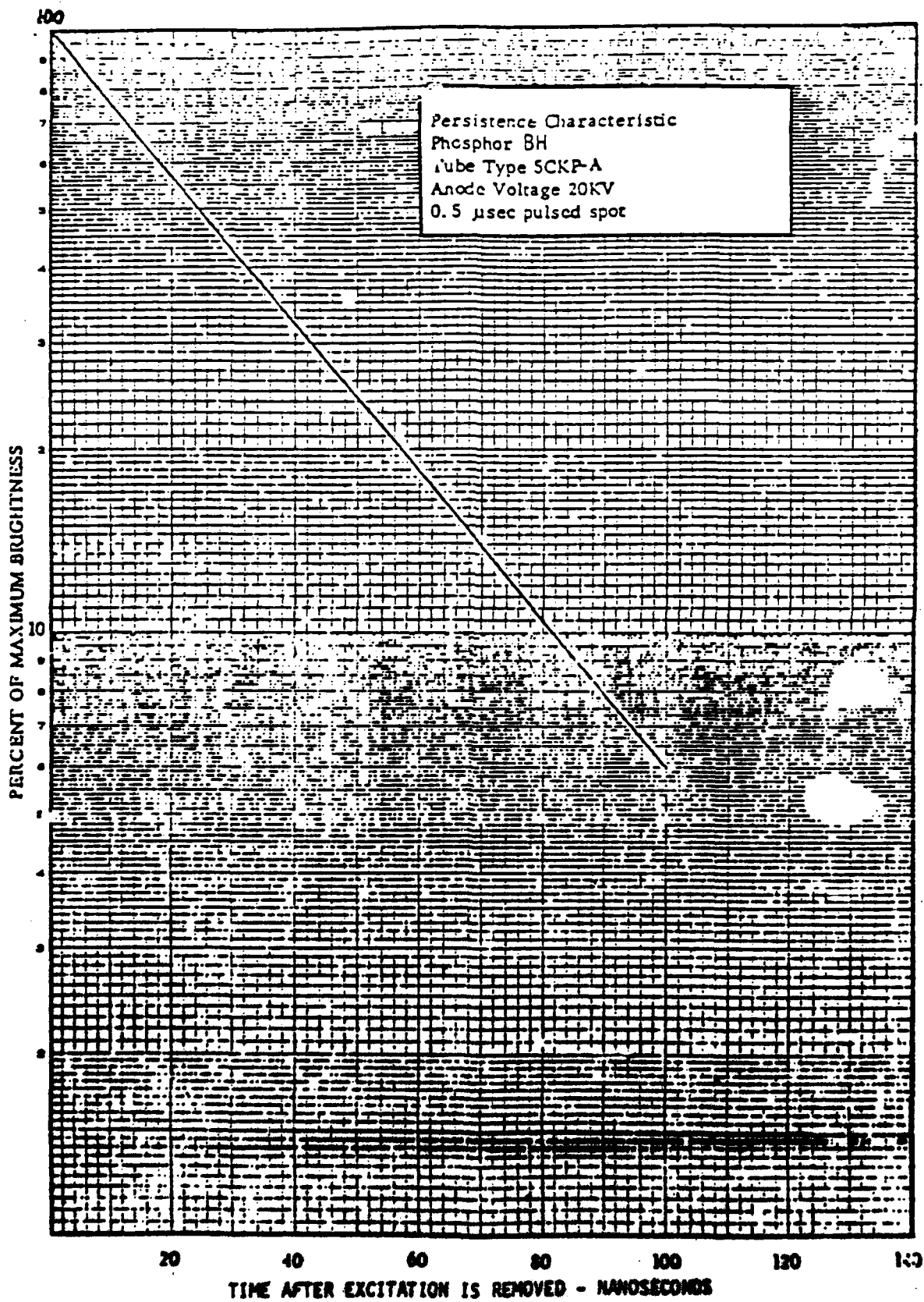
Persistence Conditions:

Comments:

	100	50	20	10	5	2	1
Nanoseconds	0	24.5	57	82	106		

50
SPECTRAL-ENERGY DISTRIBUTION CHARACTERISTICS
OF PHOSPHOR TYPE BH





52

Designation BK

Alternate or obsolete designation P37

Registration Date 3-6-67 Registrant Thomas

Color #1 Name Greenish Blue

X: .143 Y: .208 U': .110 V': .359

Color #2 Name _____

X: _____ Y: _____ U': _____ V': _____

Color #3 Name _____

X: _____ Y: _____ U': _____ V': _____

Composition Phosphor #1 Zinc sulfide: silver: nickel

Composition Phosphor #2 _____

Composition Phosphor #3 _____

Persistence (to 10% ILR)

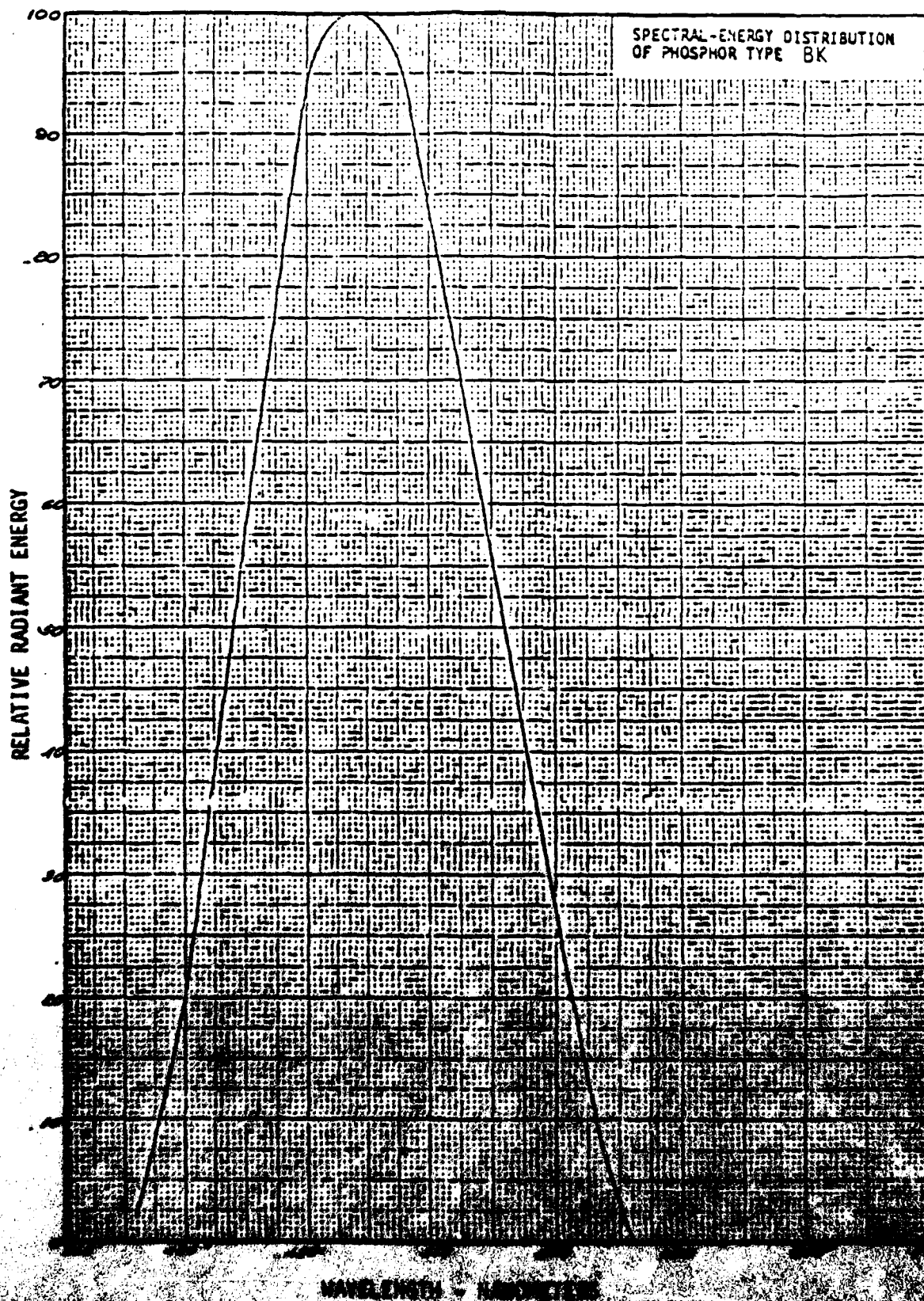
Phosphor #1 _____ Phosphor #2 _____ Phosphor #3 _____

Persistence Method: _____

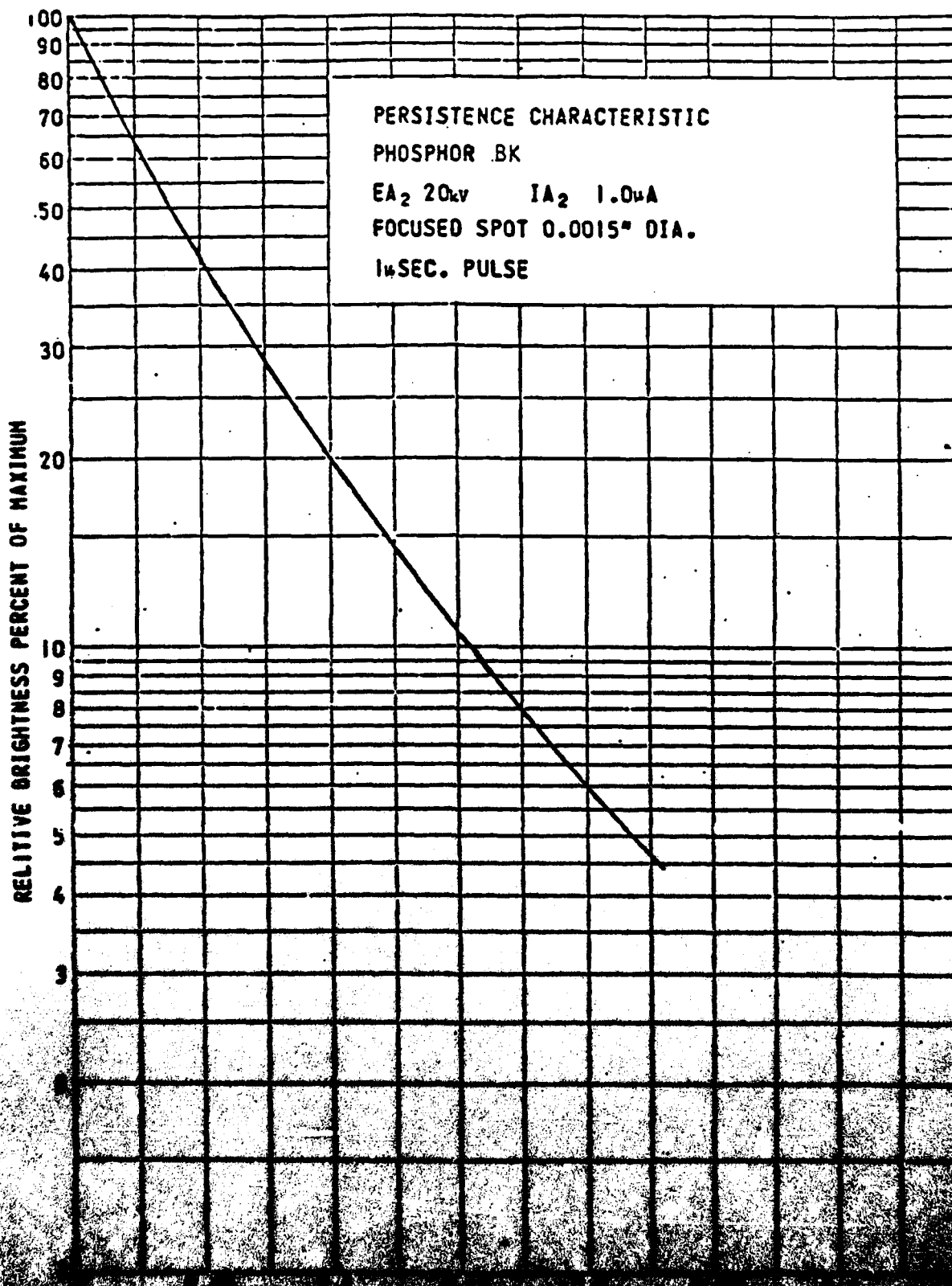
Persistence Conditions:

Comments:

	100	50	20	10	5	2	1
Microseconds	0	.04	.1	1.55	.22		



54



55

Designation GE

Alternate or obsolete designation P24

Registration Date 8-23-54 Registrant RCA

Color #1 Name _____

X: .245 Y: .441 U': .126 V': .509

Color #2 Name _____

X: _____ Y: _____ U': _____ V': _____

Color #3 Name _____

X: _____ Y: _____ U': _____ V': _____

Composition Phosphor #1 Zinc oxide

Composition Phosphor #2 _____

Composition Phosphor #3 _____

Persistence (to 10% ILR)

Phosphor #1 _____ Phosphor #2 _____ Phosphor #3 _____

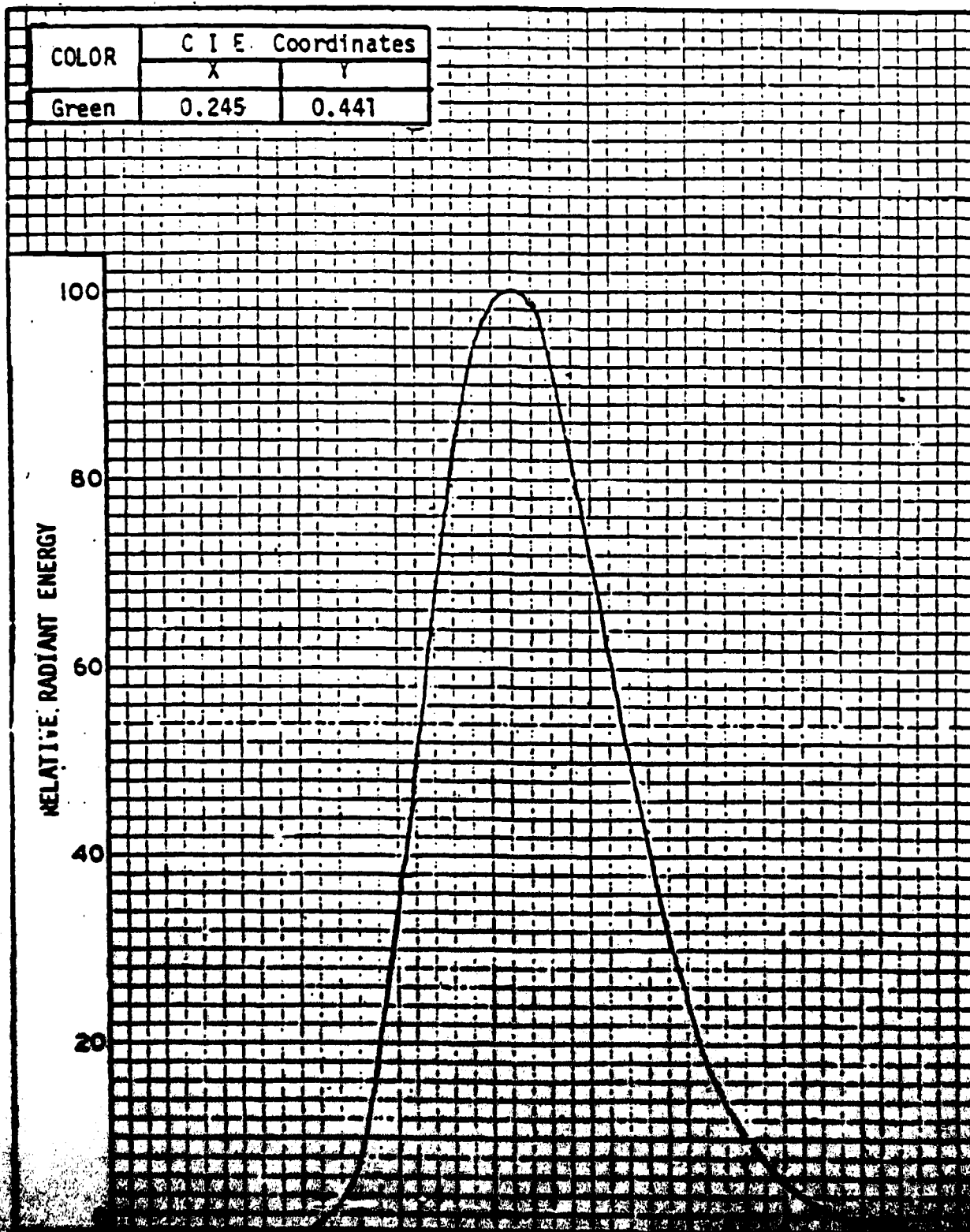
Persistence Method: _____

Persistence Conditions:

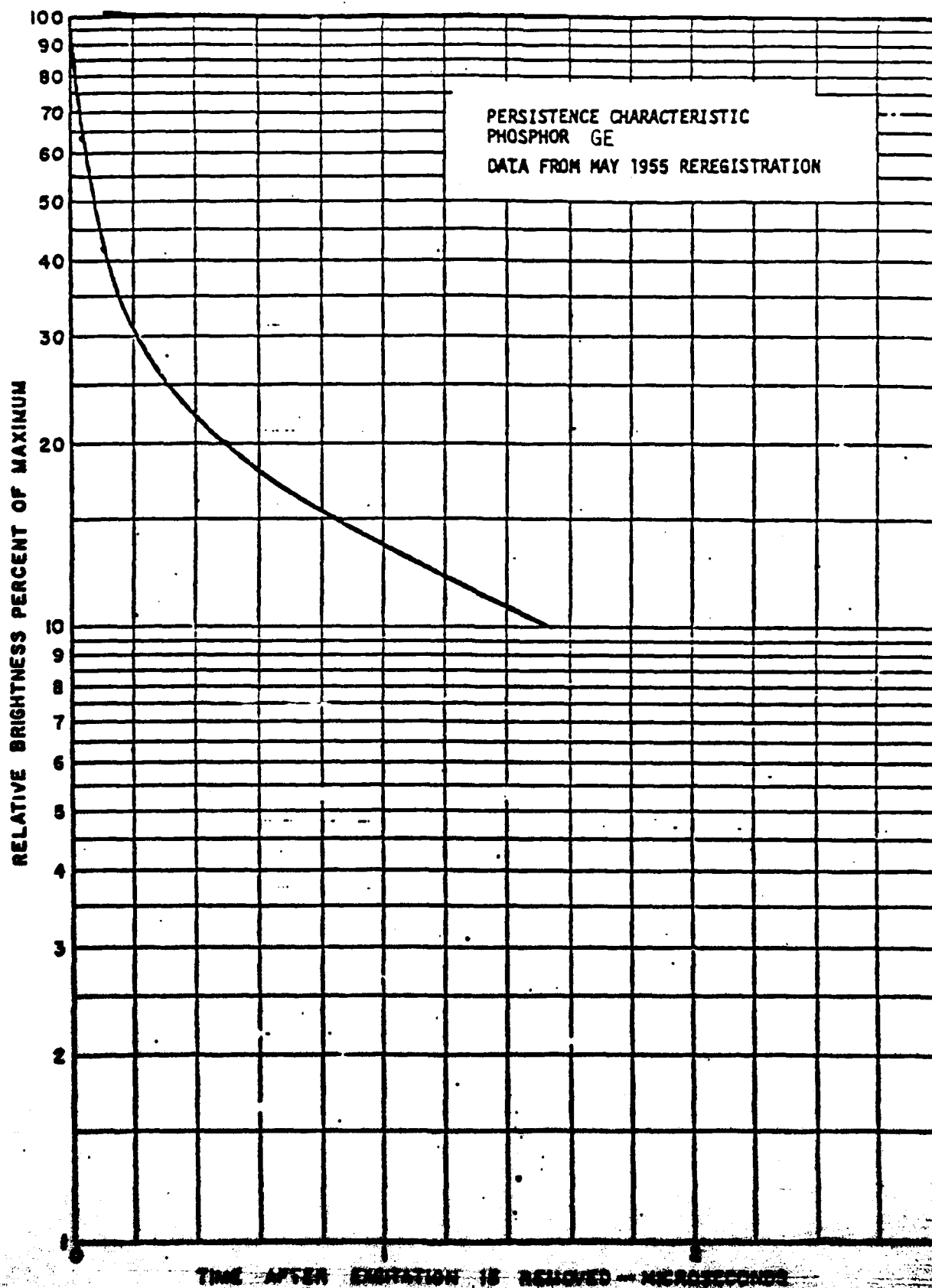
Comments:

	100	50	20	10	5	2	1
Microseconds	0	.08	.5	1.55			

SPECTRAL-ENERGY DISTRIBUTION CHARACTERISTICS
OF PHOSPHOR TYPE GE



57



58

Designation GG

Alternate or obsolete designation P15
5-16-55

Registration Date 1962 Registrant RCA AGG Telefunken

Color #1 Name Green

X: .246 Y: .439 U': .127 V': .508

Color #2 Name _____

X: _____ Y: _____ U': _____ V': _____

Color #3 Name _____

X: _____ Y: _____ U': _____ V': _____

Composition Phosphor #1 Zinc oxide

Composition Phosphor #2 _____

Composition Phosphor #3 _____

Persistence (to 10% ILR)

Phosphor #1 _____ Phosphor #2 _____ Phosphor #3 _____

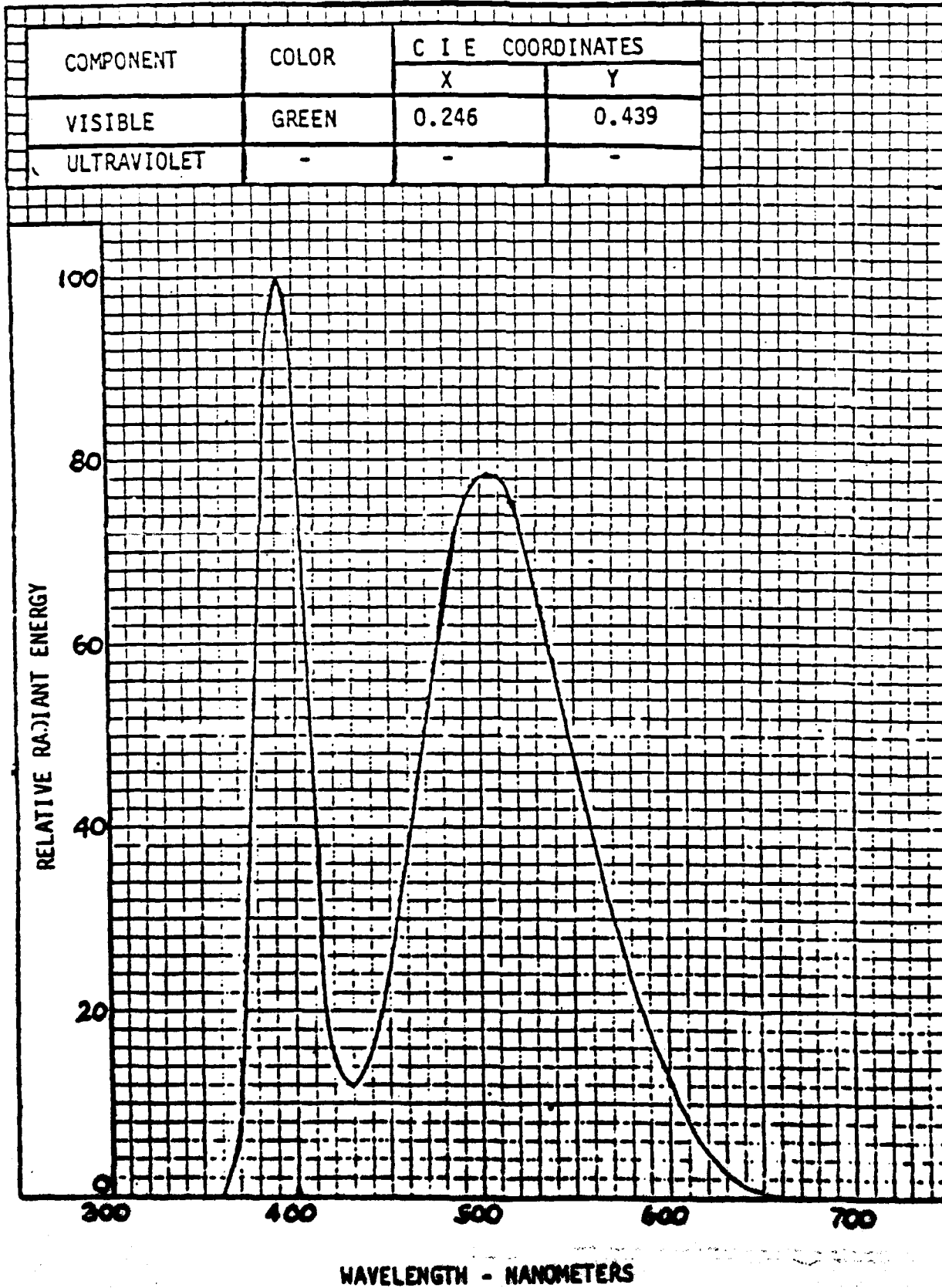
Persistence Method: _____

Persistence Conditions:

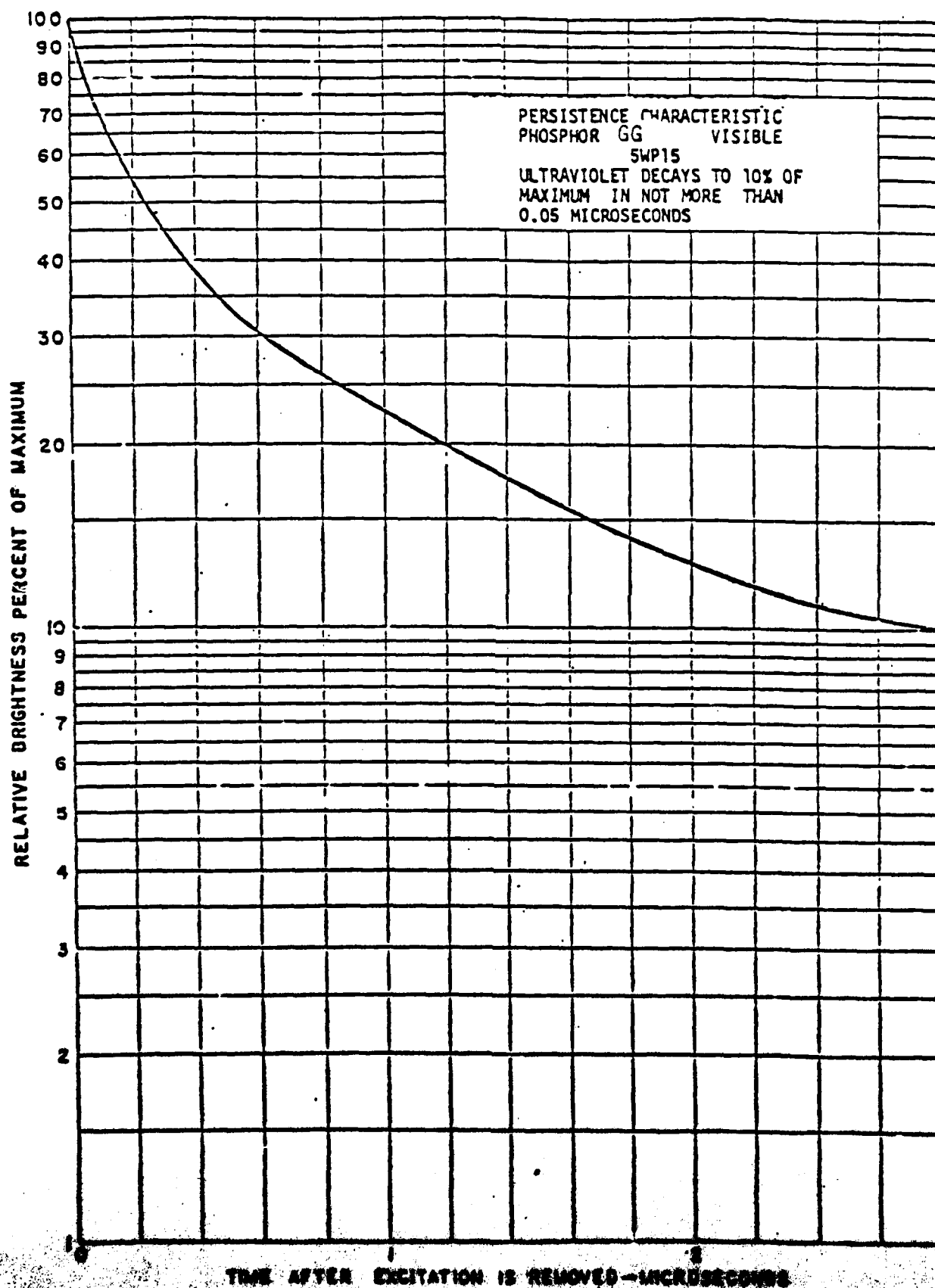
Comments:

	100	50	20	10	5	2	1
Microseconds	0	2.5	1.2	2.8			

SPECTRAL-ENERGY DISTRIBUTION CHARACTERISTICS
OF PHOSPHOR TYPE GG



60



61

Designation GS

Alternate or obsolete designation --

Registration Date 15-4-68 Registrant Thorn-Brimar

Color #1 Name Yellowish green

X: .320 Y: .530 U': .147 V': .547

Color #2 Name

X: Y: U': V':

Color #3 Name

X: Y: U': V':

Composition Phosphor #1 Zinc cadmium sulphide: Ag, Ni

Composition Phosphor #2

Composition Phosphor #3

Persistence (to 10% ILR)

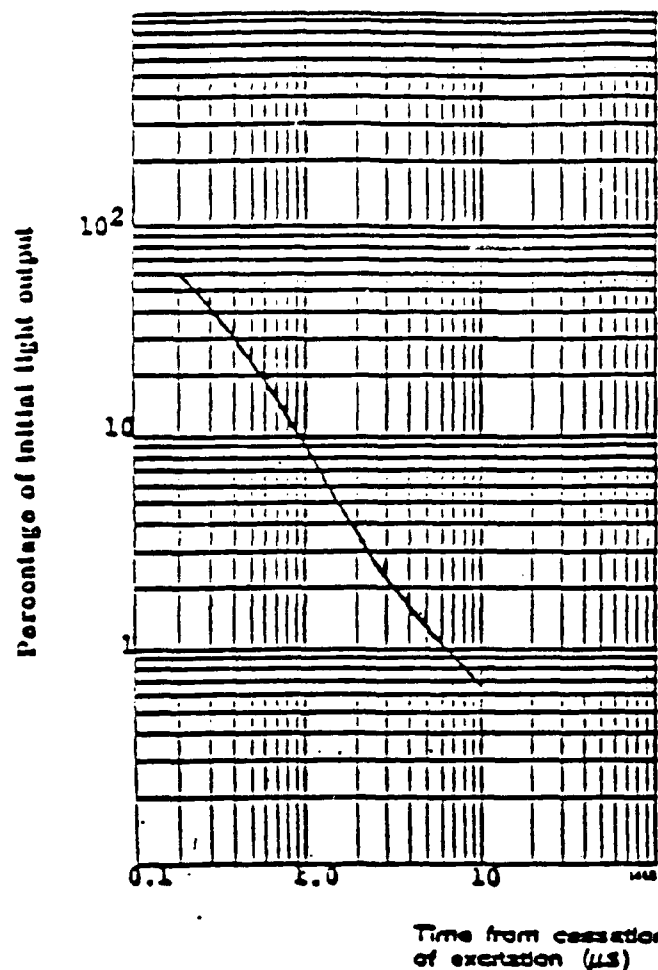
Phosphor #1 Phosphor #2 Phosphor #3

Persistence Method:

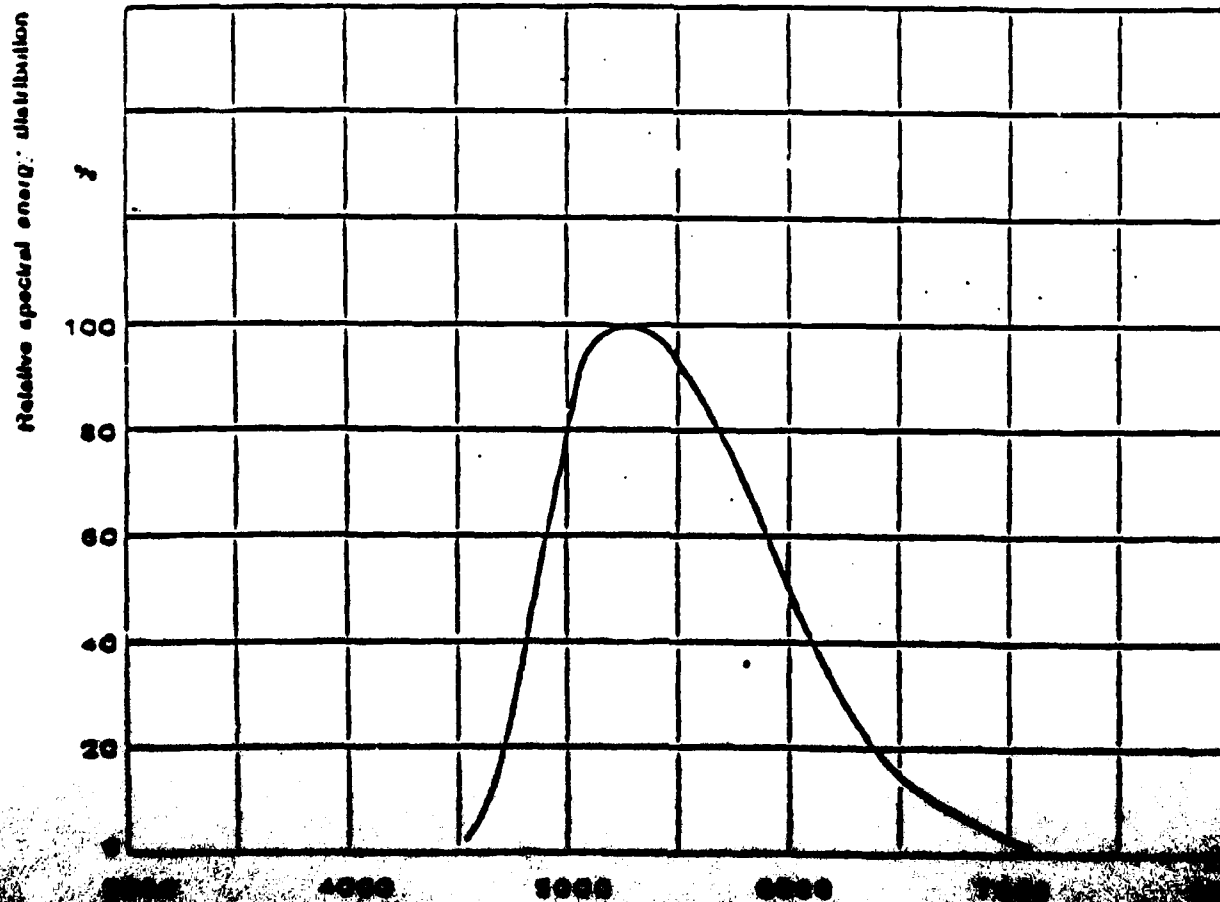
Persistence Conditions:

Comments:

	100	50	20	10	5	2	1
Microseconds	0	.25	.55	.95	1.6	3.2	6.8



Phosphor screen designation
GS
Colour
fluoresc. phosph. ICI coord.
Yellowish Yellowish $x = 0.320$
green green $y = 0.530$
Persistence (10%)
Very short
Conditions for persistence measurement
Screen voltage = 15 kV
Screen current = 4.5 μ A



63

Designation GT

Alternate or obsolete designation --

Registration Date 9-15-69 Registrant Thorn-Brimar

Color #1 Name Bluish green

X: .190 Y: .370 U': .108 V': .472

Color #2 Name

X: Y: U': V':

Color #3 Name

X: Y: U': V':

Composition Phosphor #1 Zinc cadmium sulphide: Ag, Ni

Composition Phosphor #2

Composition Phosphor #3

Persistence (to 10% ILR)

Phosphor #1 Phosphor #2 Phosphor #3

Persistence Method:

Persistence Conditions:

Comments:

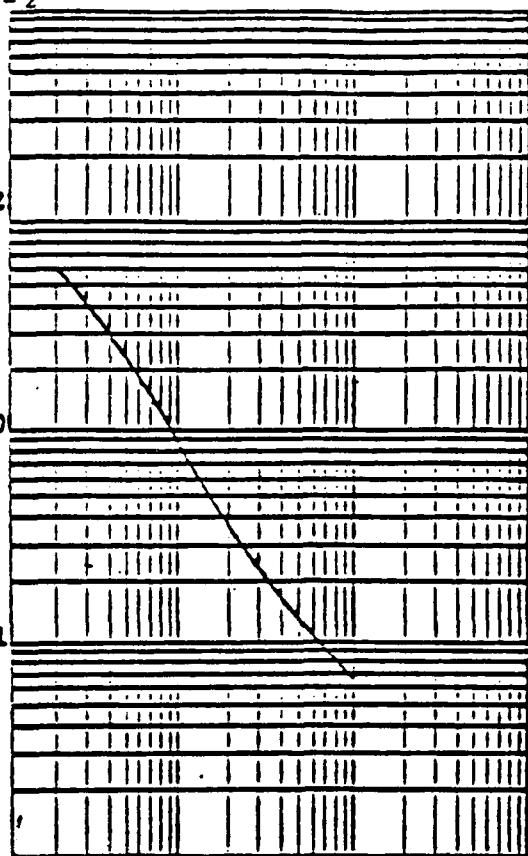
	%	100	50	20	10	5	2	1
Microseconds		0	.25	.55	.9	1.5	3.2	6.5

Percentage of initial light output

10²

10

1



0.1

1.0

10

100

Time from cessation
of excitation (μs)

Phosphor screen designation

GT

Colour

fluoresc

phosph

ICI coord

Bluish

Bluish

x = 0.190

green

green

y = 0.370

Persistence (10%)

very short

Conditions for persistence measurement

Screen voltage = 15 kV

Screen current = 4.5 μA

Relative spectral energy distribution

%

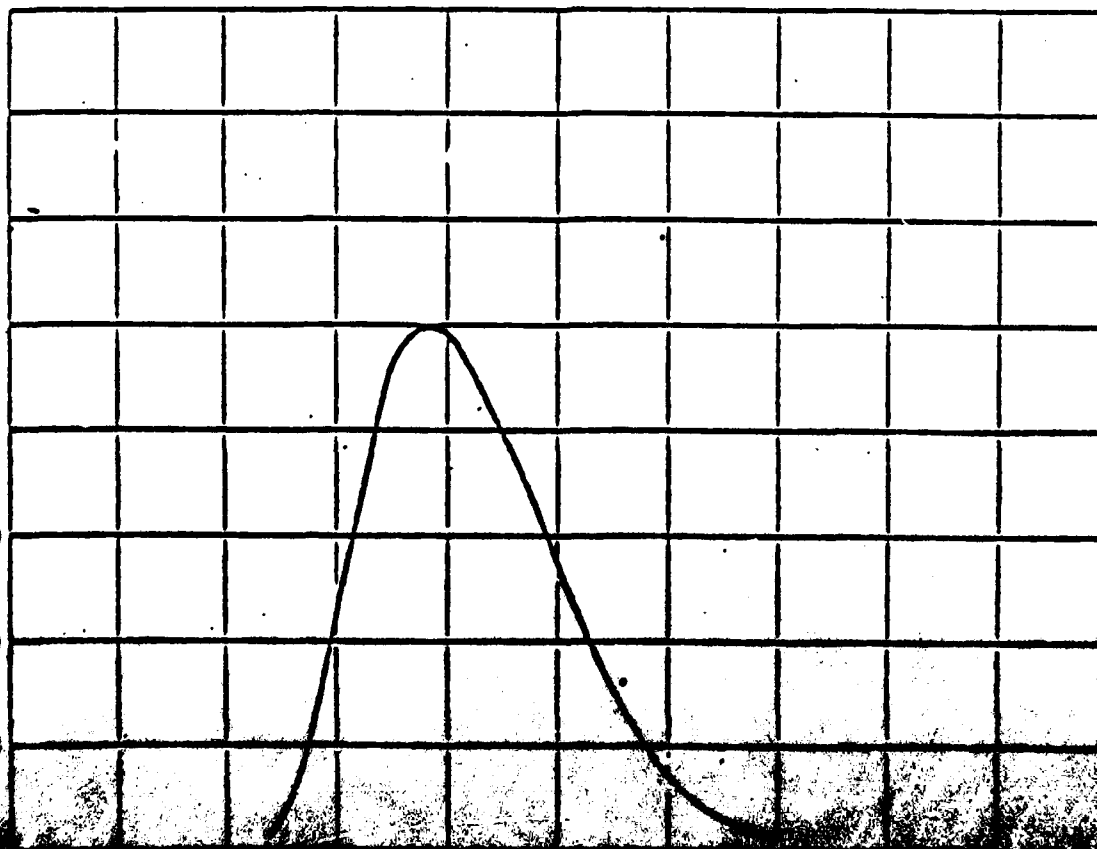
100

80

60

40

20



65

Designation GU

Alternate or obsolete designation --

Registration Date 3-16-70 Registrant Philips

Color #1 Name White

X: .297 Y: .371 U': .173 V': .487

Color #2 Name

X: Y: U': V':

Color #3 Name

X: Y: U': V':

Composition Phosphor #1 Yttrium aluminate: cerium and yttrium silicate:
cerium

Composition Phosphor #2

Composition Phosphor #3

Persistence (to 10% ILR)

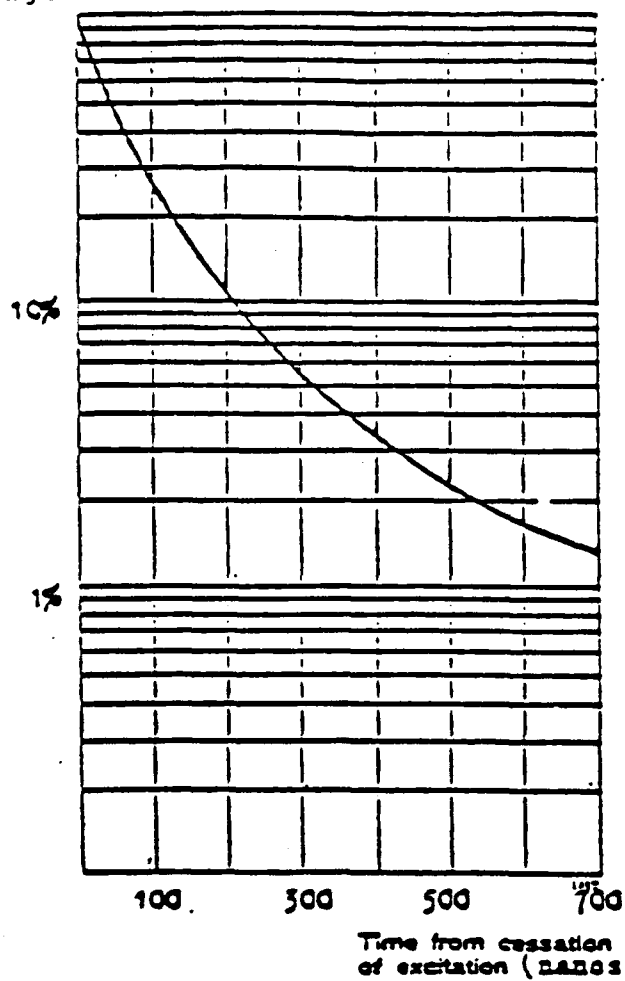
Phosphor #1 Phosphor #2 Phosphor #3

Persistence Method:

Persistence Conditions:

Comments:

%	100	50	20	10	5	2	1
Nanosec.	0	50	125	210	320	540	



Phosphor screen designation

GU

Colour

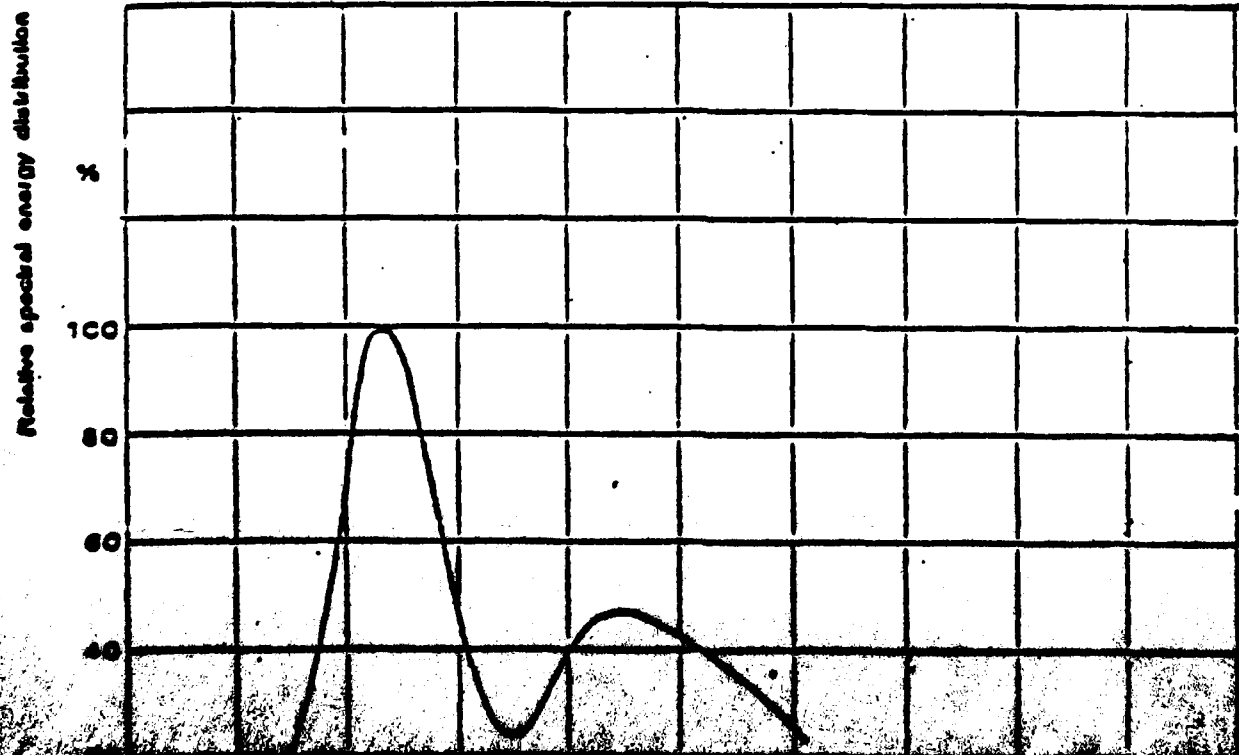
fluoresc. phosph. ICI coord.

white white $x = .297$
 $y = .371$

Persistence (10%)

very short

Conditions for persistence measurement



67

Designation KP

Alternate or obsolete designation P36

Registration Date 3-6-67 Registrant Thomas

Color #1 Name Yellow green

X: .400 Y: .543 U': .184 V': .561

Color #2 Name _____

X: _____ Y: _____ U': _____ V': _____

Color #3 Name _____

X: _____ Y: _____ U': _____ V': _____

Composition Phosphor #1 Zinc cadmium sulfide: silver: nickel

Composition Phosphor #2 _____

Composition Phosphor #3 _____

Persistence (to 10% ILR)

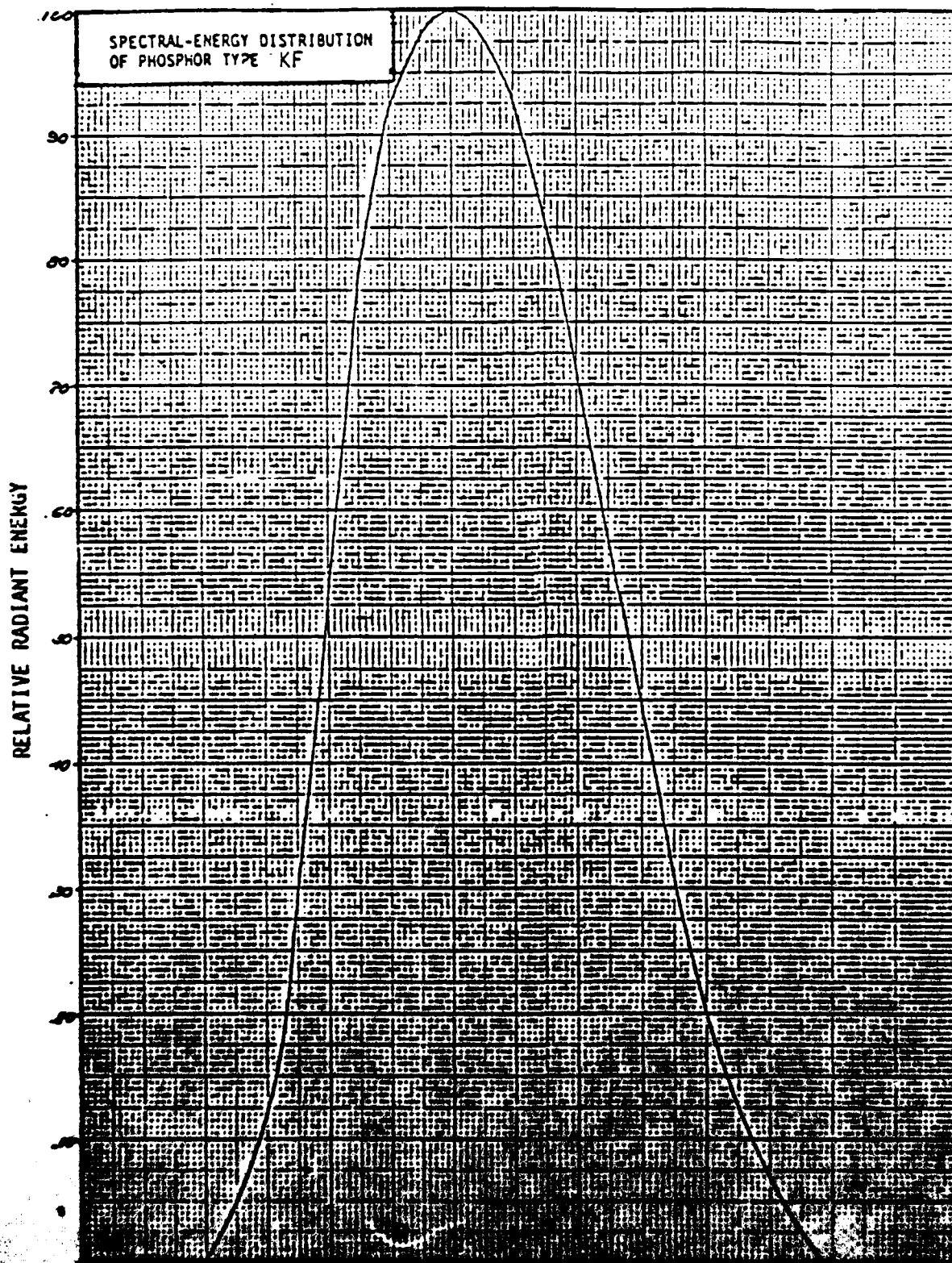
Phosphor #1 _____ Phosphor #2 _____ Phosphor #3 _____

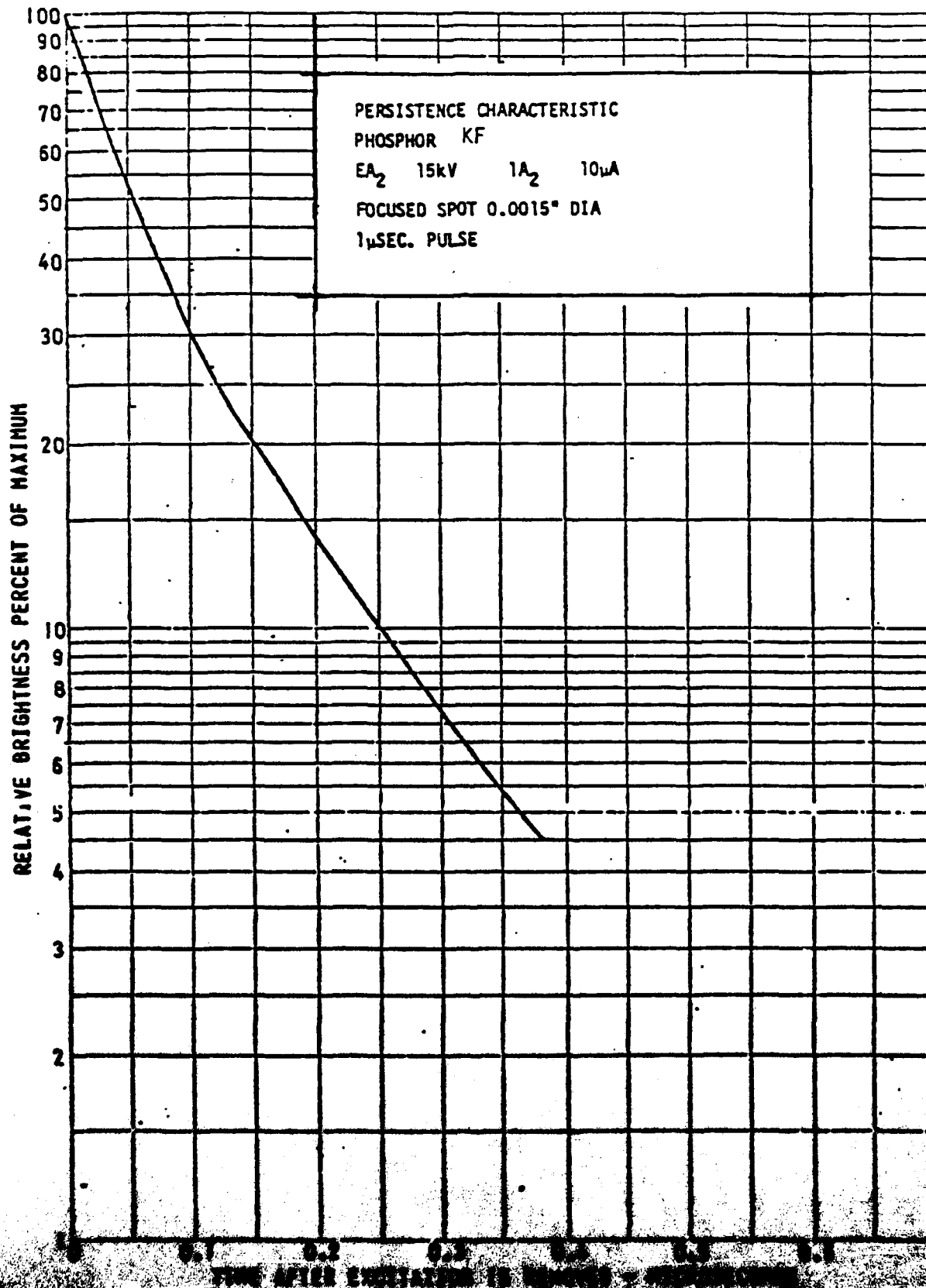
Persistence Method: _____

Persistence Conditions:

Comments:

	100	50	20	10	5	2	1
Microseconds	0	.055	.15	.25	.36		





70

Designation KG

Alternate or obsolete designation F46

Registration Date 7-17-72 Registrant Thomas

Color #1 Name Yellow green

X: .365 Y: .595 U': .155 V': .569

Color #2 Name

X: Y: U': V':

Color #3 Name

X: Y: U': V':

Composition Phosphor #1 Yttrium aluminate: cerium

Composition Phosphor #2

Composition Phosphor #3

Persistence (to 10% ILR)

Phosphor #1 Phosphor #2 Phosphor #3

Persistence Method:

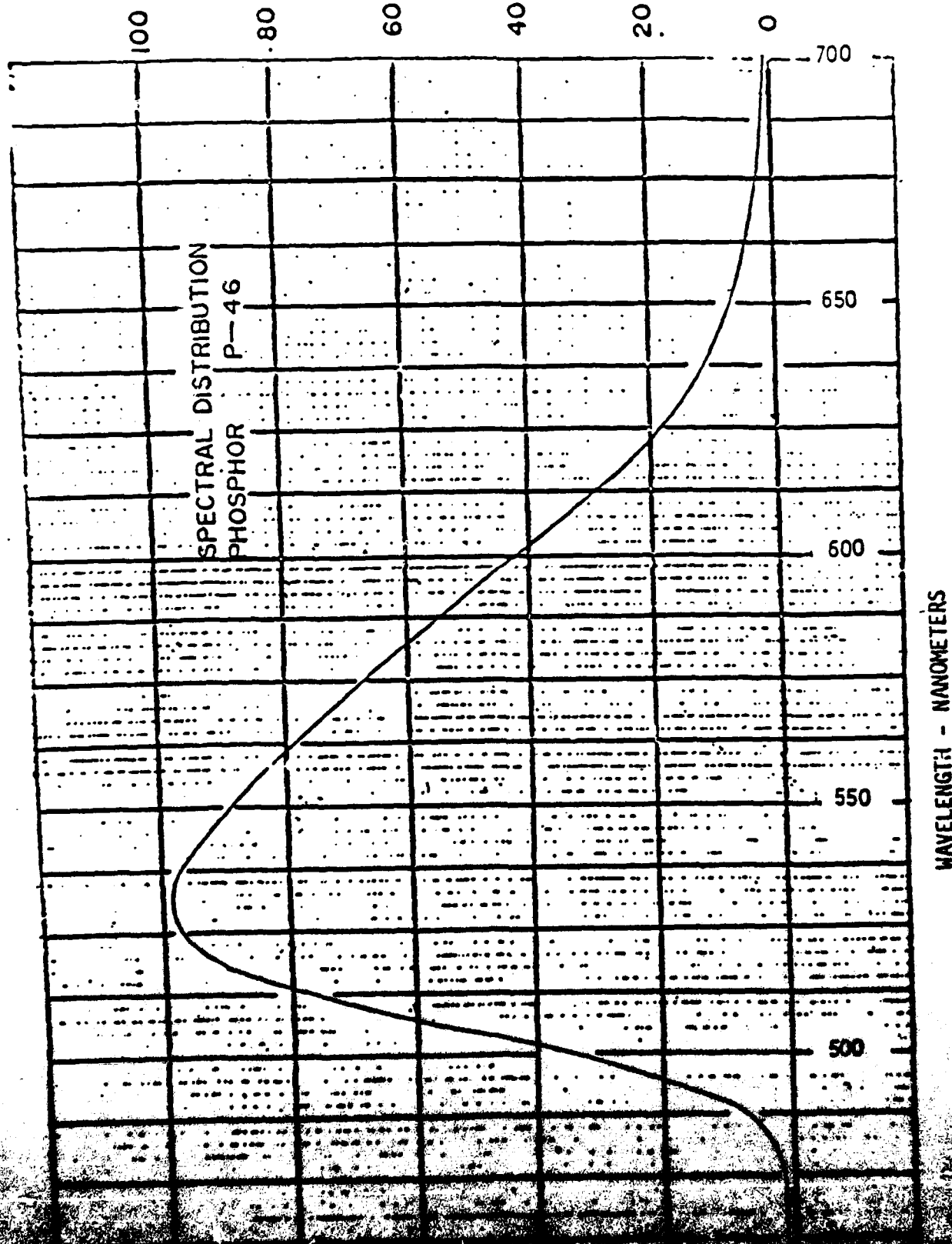
Persistence Conditions:

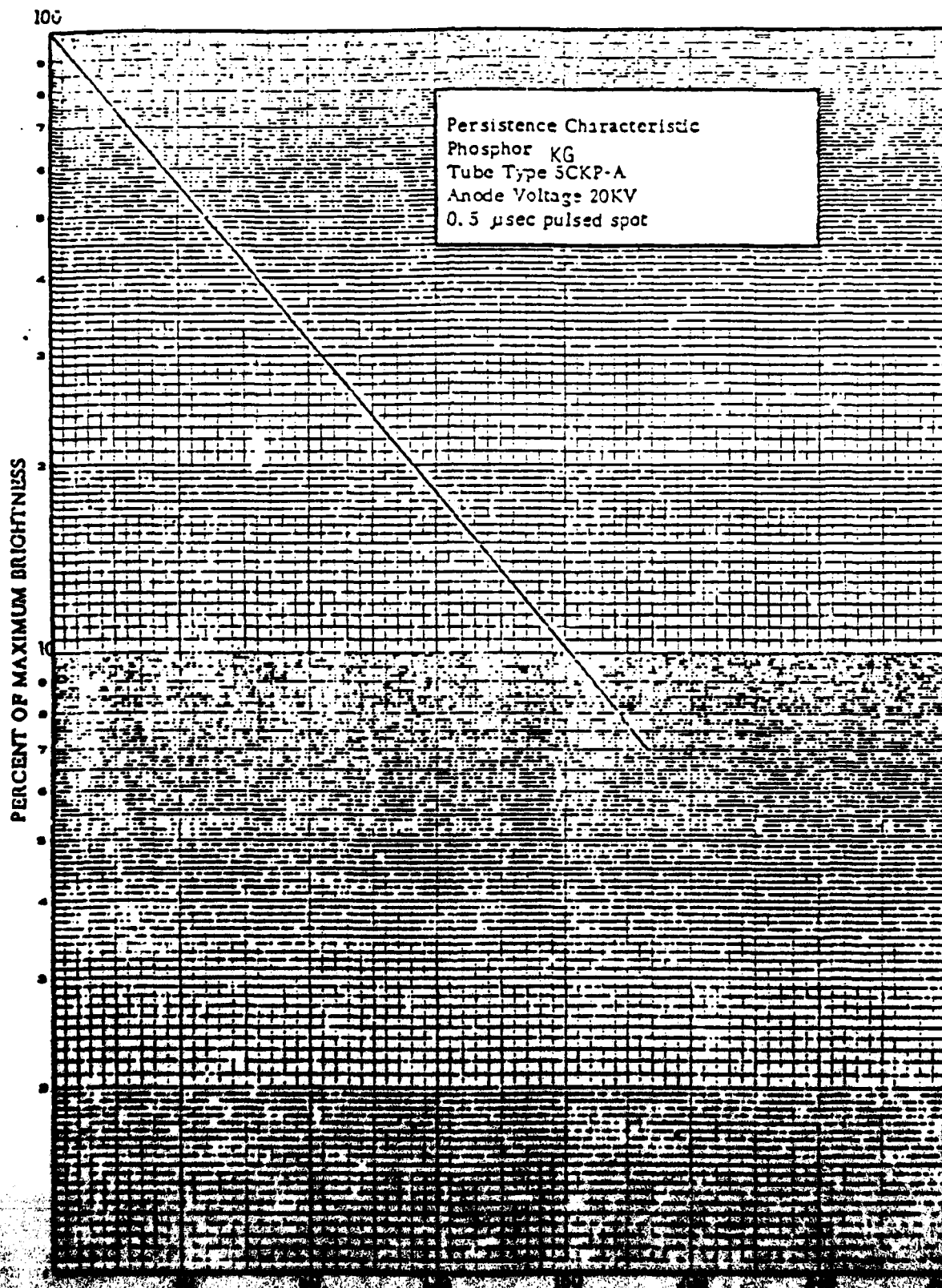
Comments:

	100	50	20	10	5	2	1
Nanosecond-	0	48	112	160			

SPECTRAL-ENERGY DISTRIBUTION CHARACTERISTICS
OF PHOSPHOR TYPE KG

RELATIVE RADIANT ENERGY





73

Designation KH

Alternate or obsolete designation P48

Registration Date 7-17-72 Registrant Thomas

Color #1 Name Yellow green

X: .365 Y: .474 U': .184 V': .536

Color #2 Name

X: Y: U': V':

Color #3 Name

X: Y: U': V':

70/30 Composition Phosphor #1 Yttrium aluminate: cerium

Composition Phosphor #2 Yttrium silicate: cerium

Composition Phosphor #3

Persistence (to 10% ILR)

Phosphor #1 Phosphor #2 Phosphor #3

Persistence Method:

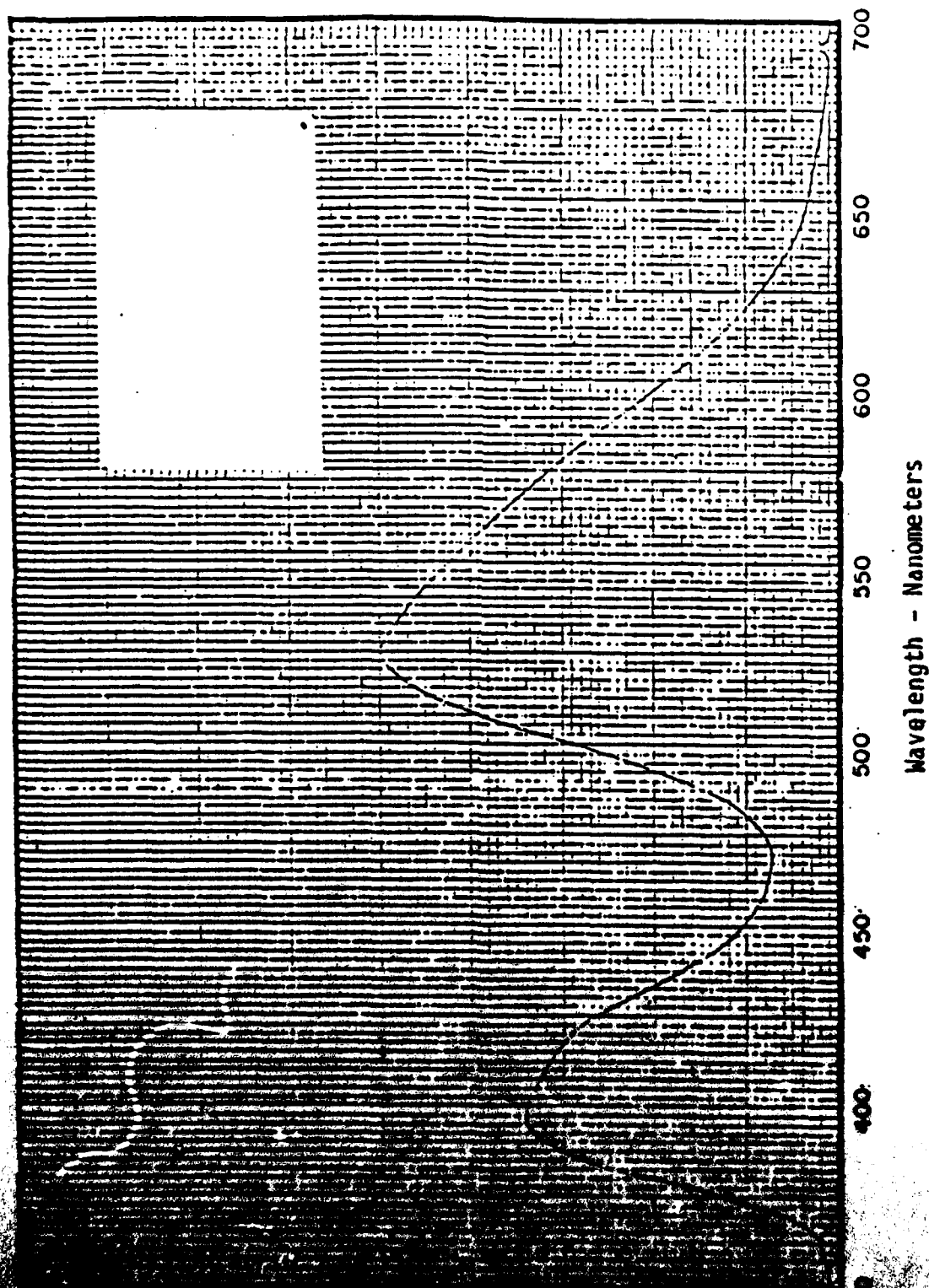
Persistence Conditions:

Comments:

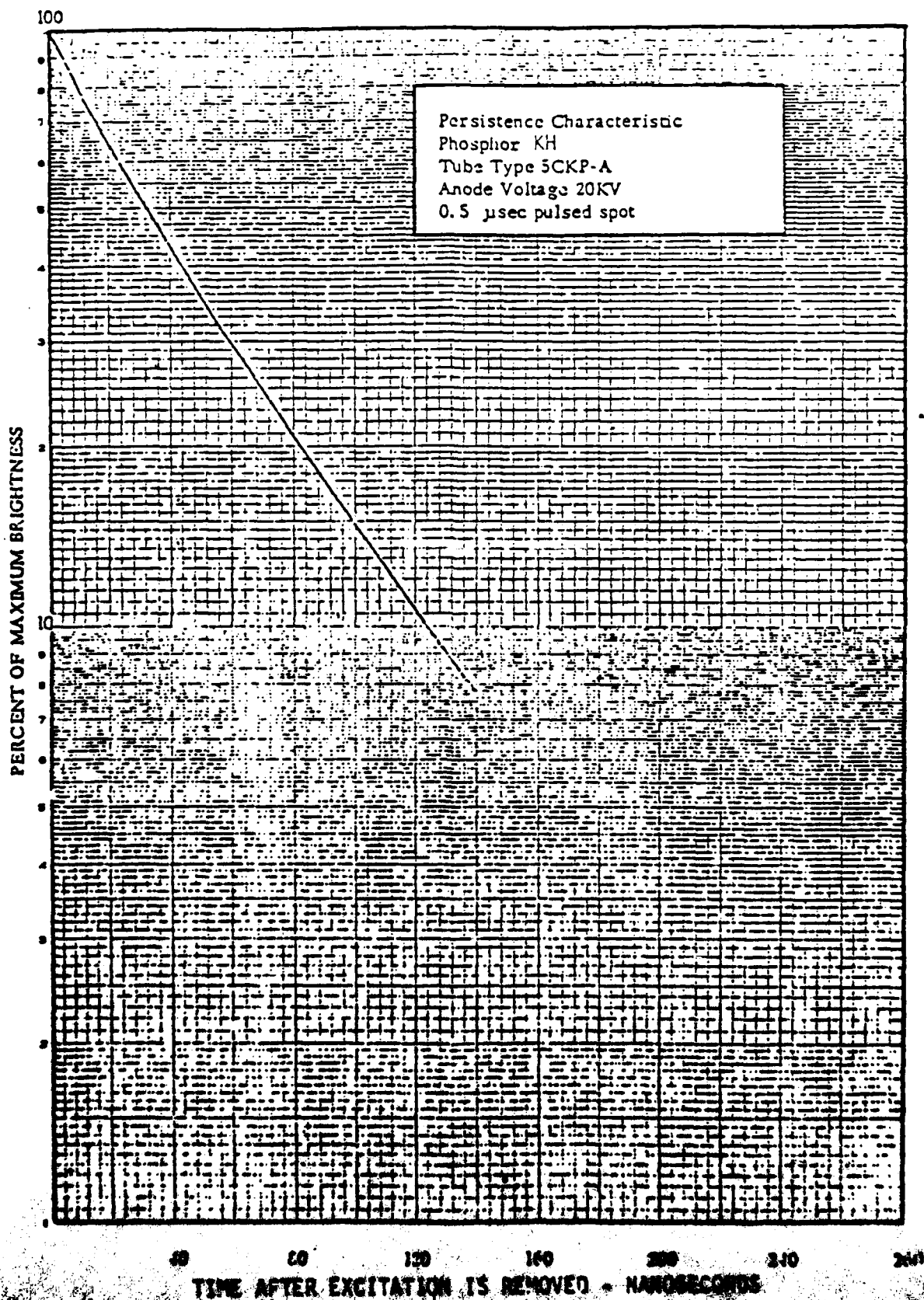
%	100	50	20	10	5	2	1
	0	32	82	124			

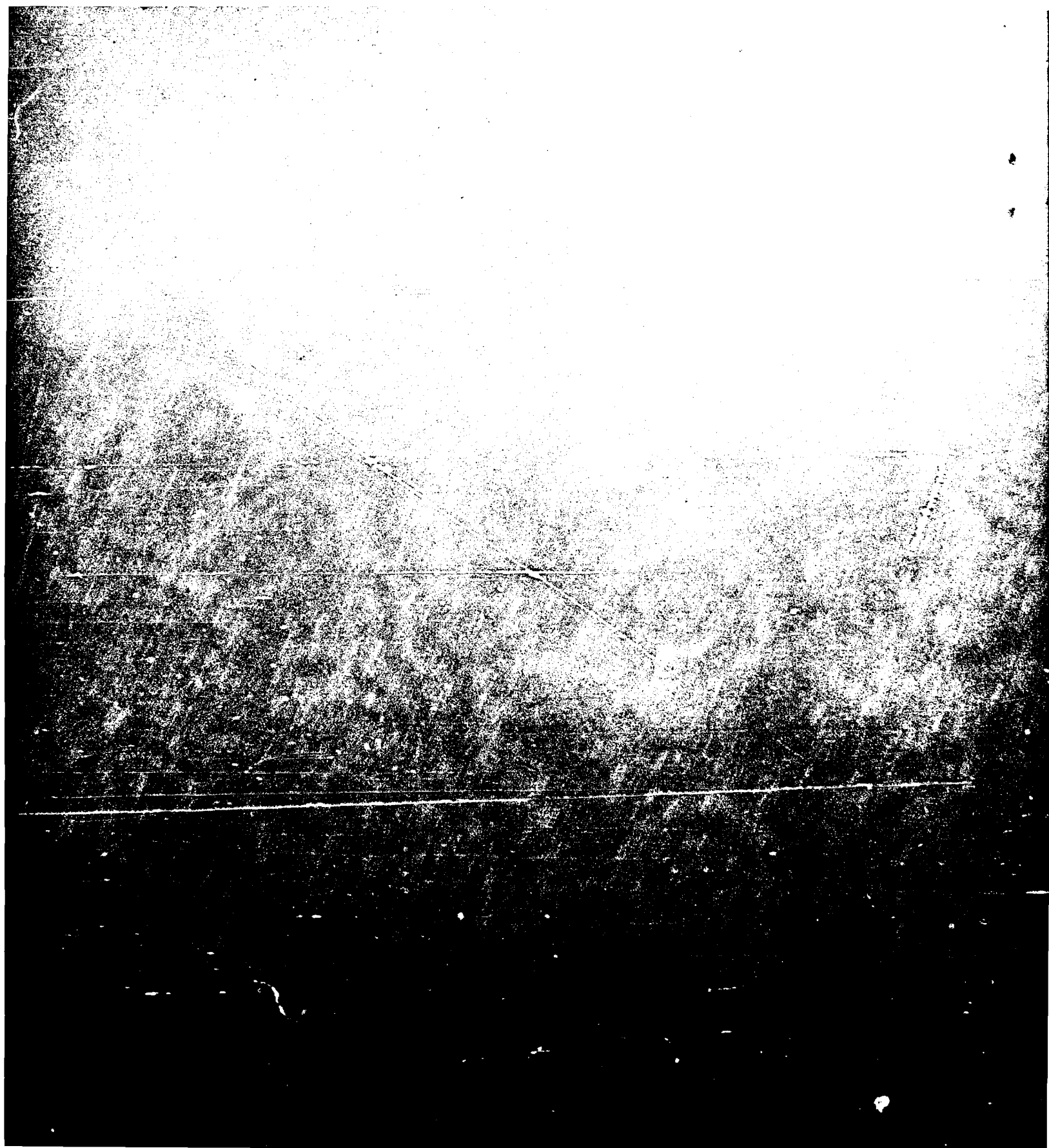
74

SPECTRAL-ENERGY DISTRIBUTION CHARACTERISTICS
OF PHOSPHOR TYPE KH



75





**END
DATE
FILMED**

9/6/89

SES